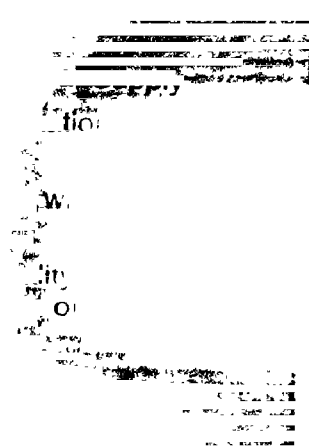
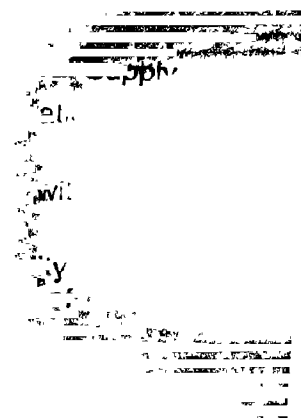


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MONTE CARLO DETERMINATION OF ELECTRON TRANSPORT PROPERTIES IN GALLIUM ARSENIDE

W. FAWCETT, A. D. BOARDMAN* and S. SWAIN
Royal Radar Establishment, Malvern, Worcestershire, England

(Received 18 August 1969; in revised form 6 October 1969)

Abstract—A Monte Carlo technique has been used to calculate the electron distribution functions in the (000) and (100) valleys of gallium arsenide. This method avoids having to make any of the conventional approximations used to solve the Boltzmann transport equation, but instead evaluates the distribution function exactly once the scattering rates have been specified. Polar, acoustic and relevant intervalley scattering processes have been included, together with the non-parabolicity and wave-vector dependence of the cell-periodic part of the Bloch functions in the (000) valley. The structure found in the distribution function in the (000) valley is interpreted in terms of the energy dependence of the scattering processes, particular reference being made to the prediction of a population inversion for fields in excess of about 10 kV/cm. The mobility, mean energy, and electron population in each valley and the mean velocity are calculated as functions of the electric field strength, and comparison is made with previous theoretical results and the experimental data.

1. INTRODUCTION

THE NEGATIVE differential mobility exhibited by *n*-type gallium arsenide at high electric field strengths has stimulated a great deal of experimental and theoretical investigation into the transport properties of this material. Many of the quantitative features of the Gunn effect [1, 2] and other instability phenomena [3, 4] which result from the negative differential mobility can be calculated from the electronic properties of gallium arsenide subject to a constant and uniform electric field, and it is therefore natural that some effort has been devoted to the determination of these static properties. In particular there have been many experimental determinations of the dependence of electron drift velocity on electric field strength and although the earlier work [5-10] gave widely different results [3], more recent work [11-13] has allowed the velocity-field relationship to be specified within much closer limits.

On the other hand, the calculation of the high-field transport properties of gallium arsenide has previously been approached by

attempting to solve the coupled Boltzmann equations for the distribution functions in the (000) and (100) minima of the conduction band, and the complicated integrodifferential form of this equation means that approximations have to be introduced to obtain a solution. Conwell and Vassell [14] have assumed the distribution functions could be represented by truncated spherical harmonic series, but this approximation is expected to be reliable in the (000) minimum only at very high fields. In the work of Butcher and Fawcett [15, 16] the distribution function was assumed to be a Maxwellian displaced in momentum space, an approximation which is only valid at electron densities much higher than commonly used in transport measurements. Consequently, it is not surprising that these two calculations have given quite different results and neither method can be regarded as reliable throughout the entire range of doping densities and electric field strengths of interest.

To circumvent the problems associated with analytic solution of the Boltzmann transport equation, numerical techniques have been recently developed to obtain an exact solution for the distribution function

*Physics Department, University of Salford, Salford, Lancashire, England.

[17-22] and in this paper we apply to gallium arsenide a generalization of the Monte Carlo technique described by Kurosawa[17], this generalization allowing complex scattering processes and band structures to be incorporated with great ease.

The principle of this method is to simulate on a computer the motion of one electron in momentum space through a large number of scattering processes taking note of the time that the electron spends in each element of momentum space during its flight, these times being proportional to the distribution function in the elements. The procedure used for following the motion of an electron requires random numbers to represent the time which the electron drifts before being scattered, and to represent the final state after the scattering event. The probability distribution for these random numbers can be completely specified in terms of the electric field strength and the transition probabilities due to the various scattering processes, but the distribution for the time of free flight becomes extremely complicated in gallium arsenide and cannot be easily related to the uniform distribution of random numbers commonly available. This difficulty has been avoided by the addition of an extra fictitious 'self-scattering' process first described by Rees[19, 20]. This extra process has the effect of giving a simple negative exponential distribution of free-flight times, as though a constant relaxation time existed, but does not alter the calculated distribution function.

In Section 2 the band structure and scattering processes used to calculate the transport properties of gallium arsenide are described. Since the behavior of high energy electrons in the (000) valley is important in this material for electric fields in excess of a few thousand volts per cm, the nonparabolicity of the (000) valley and the wave-vector dependence of the periodic part of the Bloch wave functions have been incorporated into the calculation.

In Section 3 the Monte Carlo procedure used to calculate the distribution function is

described in detail and the additional scattering process used to simplify the numerical procedure is discussed. Having obtained the distribution function, the physical observables such as the drift velocity can in principle be obtained by numerical integration. However it is more convenient to calculate these observables directly from the free-flights in the electric field, thus avoiding the necessity of accurate evaluation of the distribution function in very small cells in momentum space. The method for evaluating the observables in this direct way is also given in Section 3.

In Section 4 the results are presented. The detailed form of the distribution functions is described and interpreted in terms of the energy dependences of the scattering mechanisms. The drift velocities, carrier populations and mean energies in the (000) and (100) valleys are presented as functions of electric field strength and the dependence of these on the uncertain material parameters described. In Section 5 these results are discussed and a comparison is made with previous theoretical work and with the experimental data. Some theoretical results obtained with the Monte Carlo method using a parabolic (000) valley have been presented previously[22] and a comparison with these results is also made in Section 4.

2. THE BAND STRUCTURE AND SCATTERING MECHANISMS IN GALLIUM ARSENIDE

The minimum of the conduction band of gallium arsenide occurs at the centre of the Brillouin zone and the effective mass ratio at the bottom of the band is $m^*/m_0 = 0.067$ [23-26]. We shall assume that the valley is spherical at all energies of interest but take account of the non-parabolicity by relating the energy E to the wave-vector k through the relationship[14]

$$\frac{\hbar^2 k^2}{2m^*} = \gamma(E) = E(1 + \alpha E) \quad (2.1)$$

where

$$\alpha = \frac{1}{E_g} \left(1 - \frac{m^*}{m_0} \right)^2 \quad (2.2)$$

and E_g is the energy gap. Using $E_g = 1.52$ eV [28], α has the value 0.576 eV^{-1} in gallium arsenide.

Data concerning the subsidiary valleys in the conduction band of gallium arsenide are not yet very well established. Photoemission studies [29–31] reveal transitions to subsidiary minima about 0.35, 0.45 and 0.95 eV above the (000) minimum, and these were interpreted as being to minima at the X_1 , L_1 and X_3 points in the Brillouin zone. The identification of the lowest of these minima is consistent with the results of an analysis by Ehrenreich [32] of data on the high-temperature Hall coefficient, which showed that there are minima 0.36 eV above the (000) minimum with a combined density of states mass of about $1.2 m_0$. By analysing data on the resistivity as a function of pressure Ehrenreich was able to deduce a variation with pressure of the position of these minima relative to the valence band, and since this pressure coefficient and the above effective mass were reasonably close to the corresponding values observed in the (100) minima in silicon, Ehrenreich concluded that the subsidiary minima in gallium arsenide were probably also in the (100) directions. This conclusion is also consistent with data on gallium arsenide–phosphide alloys, which shows that the position of the (100) minima in the phosphide rich alloys extrapolated back to zero phosphorus content leads to a (000)–(100) separation of about 0.4 eV [32], and with the variation with uniaxial stress of various orientations of the threshold field for Gunn oscillations [33]. Measurements by Balslev [34] of the indirect absorption from the (000) minimum to subsidiary minima reveal minima in the (100) directions at a somewhat higher energy of 0.43 eV at 80°K, but at room temperature the data suggest that these transitions occur at a significantly lower energy. On the basis of this evidence, we have assumed that the lowest subsidiary minima lie in the

(100) directions and placed them 0.36 eV above the (000) minima. The L_1 and X_3 minima have been neglected at this stage. The neglect of the X_3 minima is justified because from the band structure calculations described below the density of states in these minima appears to be small and it seems almost certain that they are about 0.5 eV above the X_1 minima. At 0.1 eV above the X_1 minima, the justification for the neglect of the L_1 minima is not so obvious. However, as we shall see later, a reasonable choice for the strength of the various scattering processes in the X_1 valleys results in the electrons in this valley being only slightly heated by the field, so that the number of the electrons in the L_1 valleys will be small, at least until extremely high field strengths.

Although the above evidence is highly suggestive that the lowest subsidiary minima are in the (100) directions, it is worth noting that it cannot at this stage be regarded as being conclusive. The first reason for this is that Ehrenreich's analysis does not lead directly to the density of states in the subsidiary minima but to the product of the density of states and the factor $\exp(-\xi/k_B)$, where ξ is the temperature coefficient of the (000)–(100) separation and k_B is Boltzmann's constant. With ξ taken to be zero, Ehrenreich could only determine the density of states mass to lie between 0.9 and $1.7 m_0$, but these limits are drastically altered even for small temperature coefficients because of the exponential dependence on ξ . For example, if we take James' [30] recent estimate for ξ of about $-1.1 \times 10^{-4} \text{ eV}^\circ\text{K}$, then the mean density of states mass of $1.2 m_0$ given by Ehrenreich is reduced to $0.52 m_0$. More recent experiments on gallium arsenide under pressure have given the value of 0.38 eV at room temperature for the energy separation [35] of the minima and $0.85 m_0$ [36] for the density of states mass, but it is necessary in both these cases to assume either the density of states [35] or energy separation [36] to deduce these values and those given by Ehrenreich were used in these cases. Also, even if (100) minima are the lowest at high pressures in gallium arsenide, as seems almost certain, it does not necessarily follow that the (100) minima are still the lowest at zero pressure. For example, if it were the (111) minima which were slightly below the (100) minima, then since the effect of pressure would probably be to raise the former with respect to the latter, these minima could cross before the (100) started to influence the transport properties. This arrangement of the minima would not necessarily conflict with the data on the band gap in GaAs–P alloys, particularly since any non-linear variation of the band gap with composition was not taken into account in the extrapolation of the data. Also the probable proximity of the (100) and (111) minima requires that the interpretation of experiments

on the variation of the Gunn threshold field with uniaxial stress be made only at low pressures, and it is noted that it is at low pressure where the threshold field varies least.

Band structure calculations[37-42] at the present time do not consistently predict the relative positions of the (100) and (111) minima, the latter being calculated to be from as much as 0.5 eV below, to 0.4 eV above the (100) minima. Pseudopotential calculations by Cohen and Bergstresser[37] predict the (111) minima to be 0.1 eV below the (100) minima whereas Jones and Lettington[38], using the same method but a different form of the pseudopotential, have recently calculated the (111) minima to be 0.4 eV above the (100) minima. The *k*·*p* calculation of Pollak *et al* [39] places the (111) and (100) minima at about the same energy. Van Vechten[40], using a quite different approach in which dielectrically defined average covalent and ionic energy gaps are used to predict inter-band transition energies, has recently calculated the (111) minima to be 0.48 eV below the (100) minima. The (111) minima are also found to be well below the (100) minima in the OPW calculations by Collins *et al* [41], the separation being 0.44 eV, although the (100) minima occur in this case 0.8 of the way to the *X* point. On the other hand, Herman[42] has shown that it is possible to adjust the Fourier coefficients of the potential used in their OPW band structure calculation to obtain good agreement with the observed transition energies between the various minima throughout the band structure if the *X*₁ and *L*₁ minima were 0.35 and 0.45 eV respectively above the (000) minimum which are the energies observed in the photoemission experiments. Without this adjustment in the potential, there was a poorer overall fit with the data, and in particular the *L*₁ and *X*₁ minima were about 0.62 and 1.45 eV respectively above the (000) minimum.

For the calculations described below the (100) minima have been placed at the edge of the Brillouin Zone with *X*₁ symmetry as indicated by almost all the band structure calculations. However the incorporation of the ellipsoidal energy surfaces associated with *X*₁ minima is not at this stage considered to be necessary. This is primarily because of the uncertainty in the principal effective masses and because it is expected that anisotropic effects associated with these minima will be small because of strong intervalley scattering [14]. We shall therefore represent each of (100) minima by spherical energy surfaces with a scalar effective mass. As discussed above, the uncertainty in the temperature dependence of the separation of the (000) and (100) minima does not allow a reliable estimate of the density of states in the (100) valleys to be made from the high temperature Hall data. From theoretical data on gallium

arsenide and gallium phosphide[39] and experimental data on silicon, Conwell and Vassell[14] estimate that the longitudinal effective mass will be about 1.3 *m*₀, while the theoretical result for the transverse mass is 0.23 *m*₀. This leads to a density of states mass of 0.41 *m*₀ for a single (100) valley, or 0.85 for three valleys, and a conductivity mass for a (100) orientation of 0.32 *m*₀. This density of states mass is identical with that estimated by Pitt and Lees[36] from their hydrostatic pressure results using 0.36 eV for the energy separation of the (000) and (100) minima. Olechna and Ehrenreich[43] have investigated scattering by polar modes in the many-valley model and have shown that it is quite a good approximation to replace the *m*^{3/2} which appears in the expression for the polar mode limited mobility by *m*_p^{3/2} = *m*_p^{1/2}*m*_σ where *m*_p is the density of states mass and *m*_σ the conductivity mass. Using the values of *m*_p and *m*_σ given above, we obtain *m*_p = 0.34 *m*₀. It therefore seems that all the relevant masses are fairly close to each other and we have taken the value of 0.35 *m*₀ for the effective mass in the (100) valleys of gallium arsenide. It is also noted that the density of states mass in the (100) valleys of silicon is very similar, being 0.32 *m*₀.

At room temperature and low electric field strengths polar optical phonon scattering dominates in the (000) valley. For this process, the transition rate from wave-vector *k* to *k'* is given by [44, 45]

$$S_0(\mathbf{k}, \mathbf{k}') = \frac{2\pi}{\hbar} B_0(\mathbf{k}, \mathbf{k}') \times \left\{ \begin{array}{l} N_0 \delta[E(\mathbf{k}') - E(\mathbf{k}) - \hbar\omega_0] \text{ (absorption)} \\ (N_0 + 1) \delta[E(\mathbf{k}') - E(\mathbf{k}) + \hbar\omega_0] \text{ (emission)} \end{array} \right\} \quad (2.3)$$

where

$$B_0(\mathbf{k}, \mathbf{k}') = \frac{2\pi e^2 \hbar \omega_0}{V |\mathbf{k} - \mathbf{k}'|^2} \left(\frac{1}{\epsilon_r} - \frac{1}{\epsilon_0} \right) G(\mathbf{k}, \mathbf{k}'). \quad (2.4)$$

In these expressions ω_0 is the optical phonon frequency, ϵ_r and ϵ_0 are the high frequency and static dielectric constants, *V* is the volume, *N*₀ is the optical phonon occupation number,

$$N_0 = [\exp(\hbar\omega_0/k_B T) - 1]^{-1} \quad (2.5)$$

and *T* is the lattice temperature. The function

$$G(\mathbf{k}, \mathbf{k}') = \frac{1}{2} \sum_{\mu, \mu'} \int d\mathbf{r} u_{\mu, \mathbf{k}'}^*(\mathbf{r}) u_{\mu, \mathbf{k}}(\mathbf{r}) \quad (2.6)$$

is the overlap integral between the periodic parts of the Bloch functions at $\mathbf{k}$ and $\mathbf{k}'$ summed over the doubly degenerate final spin states, labelled μ' and averaged over the initial spin states μ . For free-electron plane waves or s -states $G(\mathbf{k}, \mathbf{k}') = 1$. However at large values of $\mathbf{k}$ there is an admixture of p -type valence band wave functions into the conduction band states and $G(\mathbf{k}, \mathbf{k}')$ differs from unity [44, 45]. To calculate $G(\mathbf{k}, \mathbf{k}')$ we shall use the wave functions given by Kane (Ref. [27], equation (14)) for the conduction band and simplify these by neglecting the spin-orbit splitting of the valence band. We then find that to a good approximation (see also Matz[46])

$$G(\mathbf{k}, \mathbf{k}') = (a_k a_{k'} + c_k c_{k'} \cos \beta)^2 \quad (2.7)$$

where β is the angle between $\mathbf{k}$ and $\mathbf{k}'$. The quantities a_k and c_k are given by Kane (Ref. [27], equation (15)) and in the present case reduce to the simple expressions

$$a_k = \left[\frac{1 + \alpha E(k)}{1 + 2\alpha E(k)} \right]^{1/2} \quad (2.8)$$

$$c_k = \left[\frac{\alpha E(k)}{1 + 2\alpha E(k)} \right]^{1/2} \quad (2.9)$$

For small energies we see that $a_k \rightarrow 1$ and $c_k \rightarrow 0$. We also note that to recover the usual result obtained with plane waves or s -type wave functions we simply let $\alpha \rightarrow 0$, i.e. $E_g \rightarrow \infty$, in a_k and c_k when again $a_k \rightarrow 1$ and $c_k \rightarrow 0$. The result (2.7) was obtained on the assumption that $\mathbf{k}$ was along a principal direction of the crystal (see also Ehrenreich[45] and Matz[46]). Removal of this approximation leads to unmanageable formulae, but since this is equivalent to neglecting the additional anisotropy in the scattering caused by the admixture of valence band wave functions, and this anisotropy is small in gallium arsenide, the approximation is quite good.

It is worth noting that although the results (2.1), (2.7), (2.8) and (2.9) have been derived on the assumption that the spin-orbit splitting of the valence band is negligible, the expressions as given here are still a good approximation when the spin-orbit splitting is large.

Substituting (2.4) and (2.7) into (2.3), it is straightforward to sum over all $\mathbf{k}'$ to find the total scattering rate from the state $\mathbf{k}$, i.e. the probability per unit time that an electron with wave vector $\mathbf{k}$ will be scattered; this is required for the Monte Carlo method described in the next section. The result is

$$\lambda_0(k) = \frac{em^* \omega_0}{\sqrt{2h}} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right) \frac{(1 + 2\alpha E')}{\gamma^{1/2}(E)} F_0(E, E') \times \left\{ \begin{array}{l} N_0 \text{ (absorption)} \\ (N_0 + 1) \text{ (emission)} \end{array} \right\} \quad (2.10)$$

where

$$E' = \begin{cases} E + \hbar\omega_0 \text{ (absorption)} \\ E - \hbar\omega_0 \text{ (emission)} \end{cases} \quad (2.11)$$

and

$$F_0(E, E') = C^{-1} \left(A \ln \left| \frac{\gamma^{1/2}(E) + \gamma^{1/2}(E')}{\gamma^{1/2}(E) - \gamma^{1/2}(E')} \right| + B \right) \quad (2.12)$$

$$A = [2(1 + \alpha E)(1 + \alpha E') + \alpha\{\gamma(E) + \gamma(E')\}]^2 \quad (2.13)$$

$$B = -2\alpha\gamma^{1/2}(E)\gamma^{1/2}(E') [4(1 + \alpha E)(1 + \alpha E') + \alpha\{\gamma(E) + \gamma(E')\}] \quad (2.14)$$

$$C = 4(1 + \alpha E)(1 + \alpha E')(1 + 2\alpha E)(1 + 2\alpha E'). \quad (2.15)$$

Also $\gamma(E)$ is defined by equation (2.1). To recover the result appropriate to non-parabolic bands without account being taken of the $\mathbf{k}$ -dependence of the Bloch states we let $\alpha \rightarrow 0$ in A , B and C when $A = C = 4$ and $B = 0$. To recover the parabolic result we let $\alpha \rightarrow 0$ everywhere.

Acoustic phonon scattering is also present in the (000) valley. Although this is not a very important process in this valley[14], we include it for completeness, but assume that the energy of the acoustic phonon is negligible compared with $k_B T$, and neglect the change in the electron energy during the scattering. Then, including both absorption and emission, we have[47],

$$S_n(\mathbf{k}, \mathbf{k}') = \frac{2\pi}{\hbar} B_n(\mathbf{k}, \mathbf{k}') N_n \delta[E(k') - E(k)] \quad (2.16)$$

where

$$B_n(\mathbf{k}, \mathbf{k}') = 2 \cdot \frac{\hbar \Xi_n^2}{2\rho s V} |\mathbf{k} - \mathbf{k}'| G(\mathbf{k}, \mathbf{k}') \quad (2.17)$$

and

$$N_n = \left[\exp \left(\frac{\hbar s |\mathbf{k} - \mathbf{k}'|}{k_B T} \right) - 1 \right]^{-1} \approx \frac{k_B T}{\hbar s |\mathbf{k} - \mathbf{k}'|} \quad (2.18)$$

is the phonon occupation number, ρ is the density, s is the velocity of sound and Ξ_n is the acoustic deformation potential. It is interesting to note that as the electron energy increases the effects of non-parabolicity become important before the acoustic phonon energy becomes significant in gallium arsenide at room temperature. Integrating (2.16) over all $\mathbf{k}'$ we obtain the acoustic mode scattering rate

$$\lambda_n(k) = \frac{(2m^*)^{3/2} k_B T \Xi_n^2}{2\pi \rho s^2 \hbar^4} \gamma^{1/2}(E) (1 + 2\alpha E) F_n(E) \quad (2.19)$$

where

$$F_n(E) = \frac{(1 + \alpha E)^2 + \frac{1}{2}(\alpha E)^2}{(1 + 2\alpha E)^2}. \quad (2.20)$$

To recover the result appropriate to a non-parabolic band alone we set $\alpha = 0$ in $F_n(E)$.

In the (100) valleys we shall consider polar optical, acoustic, and equivalent intervalley scattering between the (100) valleys[3, 14]. Consistent with our simple model for the (100) valleys, we shall treat the polar and acoustic scattering by the same formulae as used in the (000) valley but with $\alpha = 0$ everywhere. For equivalent intervalley scattering between parabolic, spherical valleys we have

$$S_r(\mathbf{k}, \mathbf{k}') = \frac{2\pi}{\hbar} B_r(\mathbf{k}, \mathbf{k}') \times \left\{ \begin{array}{l} N_r \delta[E(k') - E(k) - \hbar\omega_r] \text{ (absorption)} \\ (N_r + 1) \delta[E(k') - E(k) + \hbar\omega_r] \text{ (emission)} \end{array} \right\} \quad (2.21)$$

where

$$B_r(\mathbf{k}, \mathbf{k}') = (Z_r - 1) \frac{\hbar}{2\rho\omega_r V} \Xi_r^2 \quad (2.22)$$

and ω_r is the intervalley phonon frequency, Ξ_r is the deformation potential, and Z_r is the number of equivalent valleys. Assuming that the (100) valleys are at the edge of the Brillouin zone, then $Z_r = 3$. N_r is the thermal equilibrium number of phonons per mode given by

$$N_r = [\exp(\hbar\omega_r/k_B T) - 1]^{-1} \quad (2.23)$$

The integration of (2.21) over all $\mathbf{k}'$ to determine the total scattering rate due to this process gives

$$\lambda_r(k) = (Z_r - 1) \frac{m_i^{*1/2} \Xi_r^2}{\sqrt{2\pi\rho\omega_r \hbar^3}} \left\{ \frac{N_r (\text{absorption})}{(N_r + 1) (\text{emission})} \right\} \quad (2.24)$$

where

$$E_r = \begin{cases} E(k) + \hbar\omega_r (\text{absorption}) \\ E(k) - \hbar\omega_r (\text{emission}) \end{cases} \quad (2.25)$$

To calculate the transition rate due to non-equivalent intervalley scattering between the (000) and (100) valleys, it is convenient to distinguish these two types of valley by subscripts i and j . Then by analogy with (2.21) and (2.22) we have for a transition from $\mathbf{k}$ in valley i to $\mathbf{k}'$ in valley j

$$S_{ij}(\mathbf{k}, \mathbf{k}') = \frac{2\pi}{\hbar} B_{ij}(\mathbf{k}, \mathbf{k}') \times \begin{cases} N_{ij} \delta[E(k') - E_i(k) + \Delta_i - \Delta_j - \hbar\omega_{ij}] (\text{absorption}) \\ (N_{ij} + 1) \delta[E_i(k') - E_j(k) + \Delta_j - \Delta_i + \hbar\omega_{ij}] (\text{emission}) \end{cases} \quad (2.26)$$

where

$$B_{ij}(\mathbf{k}, \mathbf{k}') = \frac{\hbar}{2\rho\omega_{ij}} \Xi_{ij}^2 G_{ij}(\mathbf{k}, \mathbf{k}') \quad (2.27)$$

Consistent with our previous notation, ω_{ij} is the intervalley phonon frequency, Z_i is the number of valleys of type i , Ξ_{ij} is the intervalley deformation potential and N_{ij} is the intervalley phonon occupation number given by

$$N_{ij} = [\exp(\hbar\omega_{ij}/k_B T) - 1]^{-1} \quad (2.28)$$

It is understood in equation (2.26) that the energy is measured from the minimum of the valley denoted by the subscript; the minima are at energies Δ_i, Δ_j for valleys i, j respectively. The function $G_{ij}(\mathbf{k}, \mathbf{k}')$ in (2.27) is given by analogy with (2.7), but we now set ϵ_k to be zero for the (100) valley to be consistent with our model of these valleys. Consequently the second term in (2.7) always vanishes since either $\mathbf{k}$ or $\mathbf{k}'$ will be in a (100) valley. We then obtain, apart from a multiplicative factor representing the overlap between the (100) wave function and the s -like part of the (000) wave function which may be included in the deformation potential,

$$G_{ij}(\mathbf{k}, \mathbf{k}') = \frac{[1 + \alpha_i E_i(k)][1 + \alpha_j E_j(k')]}{[1 + 2\alpha_i E_i(k)][1 + 2\alpha_j E_j(k')]} \quad (2.29)$$

where α is zero for the (100) valleys. It is noted that $S(\mathbf{k}, \mathbf{k}')$ has been taken to be independent of $|\mathbf{k} - \mathbf{k}'|$ other than through the energy conserving delta function. This is justified on the grounds that the change in wave-vector is large, being in the order of the separation of the valley minima, and does not change much with the initial and final states within the valleys. Similarly the dependence on wave-vector of Ξ_{ij} and ω_{ij} have been neglected. Integrating (2.26) over $\mathbf{k}'$ then gives

$$\lambda_{ij}(k) = Z_j \frac{m_i^{*1/2} \Xi_{ij}^2}{\sqrt{2\pi\rho\omega_{ij} \hbar^3}} \gamma_j^{1/2}(E') (1 + 2\alpha_j E_j') F_{ij}(E, E') \times \begin{cases} N_{ij} (\text{absorption}) \\ (N_{ij} + 1) (\text{emission}) \end{cases} \quad (2.30)$$

where $F_{ij}(E, E') = G_{ij}(\mathbf{k}, \mathbf{k}')$ and

$$E_i' = \begin{cases} E_i - \Delta_i + \Delta_j + \hbar\omega_{ij} (\text{absorption}) \\ E_i - \Delta_i + \Delta_j - \hbar\omega_{ij} (\text{emission}) \end{cases} \quad (2.31)$$

As before, the function $F_{ij}(E, E')$ represents the effect of taking into account the admixture of p -functions in the (000) valley.

Finally we mention that we have completely neglected non-polar optical scattering in both the (000) and (100) valleys. For a spherical, parabolic band this process vanishes. Consequently, for the non-parabolic (000) valley considered here, it is expected that this process need only be considered at high energies, and at these energies it is probable that scattering to the (100) valleys dominates. In the (100) valleys, by analogy with silicon, it is expected that the equivalent intervalley scattering will dominate, and compared with this process, optical scattering is expected to be negligible. In any case, equivalent intervalley scattering has the same characteristics as optical scattering, and providing the strength of the former process is chosen to give the correct mobility for the (100) valleys, the neglect of optical scattering will not be serious. Also we do not consider impurity scattering. Consequently, the results described here, all of which refer to 300°K, are only applicable to material with less than about 10^{15} impurities per cm^3 , or to more heavily doped material in electric fields in excess of a few thousand V per cm.

3. THE MONTE CARLO PROCEDURE

The principle of the Monte Carlo method as applied to the determination of distribution functions is to simulate the motion of one electron in momentum space. This motion consists alternately of a drift with constant velocity in the electric field followed by a scattering by phonons. The time which the electron drifts in the electric field, the type of scattering process and the final state are

random quantities with probability distributions which can be expressed in terms of the transition rates due to the various processes and the strength of the electric field. These probability distributions, however, can be quite complex, particularly that for the drift time, whereas it is only straightforward to generate by computer random numbers with equal probability over some finite range. As a result techniques are required to convert this equal probability distribution into the complex distributions required here.

Suppose that the transition rate between two wave-vector states $\mathbf{k}$ and $\mathbf{k}'$ is $S_q(\mathbf{k}, \mathbf{k}')$. Here the subscript q denotes the scattering process and can take the values $q = 1, 2, \dots, N$, if there are N possible processes. Formulae for the $S_q(\mathbf{k}, \mathbf{k}')$ have been given in the previous section. We have not added here an extra suffix to show that the scattering rates and the number of possible processes depend on the valley we are considering, but this is to be understood throughout this section. The probability per unit time that the electron will drift for a time t in an electric field F and then be scattered is given by

$$P(t) = \lambda[\mathbf{k}(t)] \exp\left\{-\int_0^t \lambda[\mathbf{k}(t')] dt'\right\} \quad (3.1)$$

where

$$\mathbf{k}(t) = \mathbf{k}_0 + e\mathbf{F}t/\hbar, \lambda(\mathbf{k}) = \sum_{q=1}^N \lambda_q(\mathbf{k}),$$

$$\text{and } \lambda_q(\mathbf{k}) = \int d\mathbf{k}' S_q(\mathbf{k}, \mathbf{k}')$$

is the total transition rate from the state $\mathbf{k}$ due to the q 'th process. Also $\mathbf{k}_0$ is the wave vector at $t = 0$ at the beginning of the flight, i.e. the final state after the previous scattering event.

The procedure adopted by Kurosawa[17] to generate random times from the probability distribution (3.1) was to use random numbers r generated with equal probability between 0 and 1. Then using $P(r) dr = P(t) dt$ we obtain

$$r = \int_0^t P(t') dt'$$

or

$$r = 1 - \exp\left\{-\int_0^t \lambda[\mathbf{k}(t')] dt'\right\}. \quad (3.2)$$

For some scattering processes the integral in (3.2) can be evaluated analytically and t determined from a random number r analytically or numerically. However, the complicated form of $S_q(\mathbf{k}, \mathbf{k}')$ for some of the scattering processes considered here means that the integral cannot be evaluated analytically and t can then be determined from r only by solving the integral equation or by interpolation in a numerical table of λ as a function of t and the initial components of $\mathbf{k}$.

Instead of these possibilities an alternative technique has been used to generate times from the distribution (3.1). Suppose in addition to the real scattering processes present in the semiconductor we include a fictitious process[19, 20] for which

$$S_0(\mathbf{k}, \mathbf{k}') = \lambda_0(\mathbf{k})\delta(\mathbf{k} - \mathbf{k}'). \quad (3.3)$$

Since the delta function does not allow the electron wave vector to change in the scattering event, this 'self-scattering' process is of no physical significance and then the function $\lambda_0(\mathbf{k})$ is completely arbitrary. Including this additional process in equation (3.1) leads to

$$P(t) = \{\lambda_0[\mathbf{k}(t)] + \lambda[\mathbf{k}(t)]\} \times \exp\left\{-\int_0^t (\lambda_0[\mathbf{k}(t')] + \lambda[\mathbf{k}(t')]) dt'\right\} \quad (3.4)$$

and we can now choose $\lambda_0(\mathbf{k})$ in such a way that the exponential factor becomes simple. The particular choice which has been made for $\lambda_0(\mathbf{k})$ in the present work is

$$\lambda_0(\mathbf{k}) = \Gamma - \lambda(\mathbf{k}) \quad (3.5)$$

where Γ is constant. This choice for $\lambda_0(\mathbf{k})$, while not necessarily the optimum expression, has the advantage that (3.4) becomes simply

$$P(t) = \Gamma e^{-\Gamma t} \quad (3.6)$$

and so has the effect of simulating the motion of an electron that has an energy-independent relaxation time of $1/\Gamma$. The constant Γ is taken to be at least as large as the largest value of $\lambda(\mathbf{k})$ of interest in order to avoid negative values of $\lambda_0(\mathbf{k})$.

The effect of including the self-scattering process is to subdivide the real flight of the electron into shorter flights of duration governed by the probability distribution (3.6). It is possible to see this in an entirely mathematical way by writing the original probability distribution (3.1) in the form

$$P(t) = \lambda(t) e^{-t/\tau} \exp \left\{ \int_0^t [\Gamma - \lambda(t')] dt' \right\} \quad (3.7)$$

where for simplicity we have written $\lambda[\mathbf{k}(t)]$ as $\lambda(t)$. Expanding the second exponential factor we obtain

$$\begin{aligned} P(t) = & \lambda(t) e^{-t/\tau} \left\{ 1 + \int_0^t [1 - \lambda(t')] dt' + \frac{1}{2!} \right. \\ & \times \left\{ \int_0^t [1 - \lambda(t')] dt' \right\}^2 + \dots \left. \right\} \\ = & \lambda(t) e^{-t/\tau} + \int_0^t dt' e^{-t'/\tau} [1 - \lambda(t')] e^{-t/\tau} \lambda(t) \\ & + \int_0^t dt' \int_0^{t'} dt'' e^{-t''/\tau} [1 - \lambda(t')] e^{-t/\tau} \lambda(t) \\ & \times [1 - \lambda(t')] e^{-t'/\tau} \lambda(t) + \dots \end{aligned} \quad (3.8)$$

The various terms in the expansion (3.8) can now be clearly identified as being the probability of the electron suffering 0, 1, 2, ... self-scattering events during its real flight of duration t . Alternatively, this proof shows that the introduction of self-scattering does not alter the distribution (3.1) of times of flights terminated by a real scattering process.

Having determined the time of free flight, it is necessary to determine the scattering process responsible for terminating the flight. Since the probability of the electron being scattered by process q is proportional to $\lambda_q(\mathbf{k})$, and since $\sum_{q=0}^N \lambda_q = \Gamma$, it is only necessary to generate a random number s between 0 and Γ and test the inequality

$$s < \sum_{q=0}^m \lambda_q(\mathbf{k}) \quad (3.9)$$

for all m . When this inequality is satisfied, the scattering process m is selected. It is at this stage that the only disadvantage of using the simple distribution (3.6) is made apparent, because there is now a finite probability of self-scattering being selected. Since this

process does not change the electron wave-vector, it does not contribute to the determination of the distribution function. It is clearly an advantage to make Γ as small as possible in order to make the number of self-scattering events a minimum. Despite this disadvantage, it is still more efficient to include self-scattering than to work directly with the distribution (3.1), particularly since the final state after the self-scattering is known.

For all real processes, further random numbers are required to determine the final state after the scattering. It is convenient to regard phonon absorption and emission as separate processes in (3.9). Then the energy of the final state is also determined by this inequality for all the processes considered here, since the energy change is either independent of the change in momentum, as in polar and intervalley scattering, or zero as in acoustic scattering. We note that this would not be the case if the acoustic phonon energy were kept finite, when a more complicated procedure would be required. However, in the present case, it then only remains to determine the components of $\mathbf{k}$ corresponding to this energy after the scattering event.

The procedure for calculating these components of the wave-vector $\mathbf{k}'$ after scattering is simplified by noting that the distribution function will be symmetric about the field direction for the band structure considered here. Hence only those components parallel and perpendicular to the electric field are needed and we denote these by k'_z and k'_ρ respectively. Acoustic scattering in the (100) valley and all the intervalley scattering processes are randomizing, so that once the energy of the final state has been determined, all states on that energy surface are equally probable final states (see equations 2.16 (with $G = 1$) 2.21 and 2.26). Hence the probability that the angle between $\mathbf{k}'$ and the field direction z has some value θ is proportional to the number of states on a circle with radius $|\mathbf{k}'| \sin \theta$. We can then write $P(\theta) = A \sin \theta$ where A is a normalizing con-

stant. If r is a uniformly distributed random number between 0 and 1 we then have

$$r = \int_0^\theta P(\theta) d\theta = 1/2(1 - \cos \theta) \quad (3.10)$$

and then $k'_\rho = |k'| \sin \theta$, $k'_z = |k'| \cos \theta$.

For polar and acoustic scattering in the (000) valley and polar scattering in the (100) valleys such a simple procedure is not possible because of the more complicated angular probability distribution. It is more convenient in these cases to first determine the angle β between $\mathbf{k}$ and $\mathbf{k}'$. For polar scattering in the (100) valleys equation (2.4) with $\alpha = 0$ gives

$$P(\beta) d\beta \sim [E + E' - 2(EE')^{1/2} \cos \beta]^{-2} \times \sin \beta d\beta.$$

Again using random numbers r equally distributed between 0 and 1 then gives the relationship

$$r = \int_0^\beta P(\beta) d\beta = \ln [1 + f(1 - \cos \beta)] / \ln [1 + 2f]$$

or solving for $\cos \beta$

$$\cos \beta = [(1 + f) - (1 + 2f)^r] / f \quad (3.11)$$

where $f = 2(EE')^{1/2}(E^{1/2} - E'^{1/2})^{-2}$. When β has been determined from (3.11), a further random number between 0 and 2π determines the azimuthal angle and then $\mathbf{k}'$ is completely specified.

For polar and acoustic scattering in the (000) valley equations (2.4) and (2.16) give

$$P(\beta) d\beta \sim \frac{[\gamma^{1/2}(E)\gamma^{1/2}(E') + \alpha EE' \cos \beta]^2}{[\gamma(E) + \gamma(E') - 2\gamma^{1/2}(E)\gamma^{1/2}(E') \cos \beta]} \sin \beta d\beta \quad (3.12)$$

and

$$P(\beta) d\beta \sim [1 + \alpha E(1 + \cos \beta)]^2 \sin \beta d\beta \quad (3.13)$$

respectively. For these probability distributions it is not possible to deduce an expression

for β as an explicit function of a uniformly distributed random number. We have therefore used a technique due to von Neumann to generate random numbers from the distributions (3.12) and (3.13). We note from these equations that $P(\cos \beta) = P(\beta)/\sin \beta$ is a monotonically increasing function of $\cos \beta$ in the range -1 to 1 with a maximum value of $P(1)$ at $\cos \beta = 1$. Random numbers were therefore generated in pairs, the first number r_1 representing $\cos \beta$ in the range -1 to 1 , and the second number r_2 was generated between 0 and $P(1)$. If r_2 was less than $P(r_1)$ then r_1 was taken as the value of $\cos \beta$. If r_2 was greater than $P(r_1)$ a second pair of random numbers were generated and the process repeated. It is clear that the accepted values of r_1 follow the required probability distribution.

In order to determine the distribution functions in the (000) and (100) valleys histograms are set up in (k_z, k_ρ) space where k_z is parallel to the electric field. Under the influence of the electric field k_ρ remains constant while k_z increases according to $dk_z/dt = eF/\hbar$. Counts proportional to the time that the electron spends in each cell of the histogram are then recorded during the course of the free flights in the electric field. The transitions between states due to the various scattering processes are of course taken to be instantaneous. Separate histograms are set up for the (000) and (100) valleys and the electron switches from one histogram to the other when an intervalley scattering takes place. The ratio of the times that the electron spends in the two histo-

grams is equal to the ratio of electron populations in the two valleys. The time that the electron spends in a particular cell is proportional to the distribution function at this point in (k_z, k_ρ) space.

Once the distribution function has been

calculated, the physical observables of interest such as the drift velocity, mean energy, etc. can in principle be obtained by numerical integration. However, in order to avoid having to use a fine histogram mesh to achieve the desired accuracy, it is more convenient to calculate these quantities directly from the initial and final $\mathbf{k}$ -components of each free-flight. Thus the drift velocity in valley j , for example, is given by

$$v_j = \frac{1}{K_j} \sum \int_{k_{zi}}^{k_{zf}} \frac{1}{\hbar} \frac{\partial E}{\partial k_z} dk_z = \frac{1}{\hbar K_j} \sum (E_f - E_i) \quad (3.14)$$

where k_{zi} and k_{zf} are the initial and final values of k_z for a particular flight, K_j is the total length of the $\mathbf{k}$ -space trajectory in the valley and is related to the total time T_j which the electron spends in the valley through $T_j = \hbar K_j / eF$. The summation in (3.14) is over all electron free-flights in the valley. E_i and E_f are the initial and final energies for the flight. The quantity $1/K_j$ may be interpreted as the distribution function per unit length of the $\mathbf{k}$ -space trajectory

4. RESULTS

All of the parameters required to specify the scattering rate in the (000) valley due to polar optical phonons are well-known in gallium arsenide. The longitudinal optic phonon frequency at the centre of the zone ω_0 is 5.37×10^{13} rad. sec⁻¹ [48] and the static and high frequency dielectric constants are $\epsilon_0 = 12.53$ and $\epsilon_\infty = 10.82$ respectively [28]. As discussed in Section 2, the coefficient α required to describe the (000) band is 0.576 eV⁻¹, while the effective mass ratio at the bottom of the band is 0.067 [23–26]. The acoustic deformation potential Ξ_u in the (000) valley was taken to be 7 eV [32, 49], and the remaining parameters needed to calculate the acoustic phonon scattering rate are the velocity of sound $s = 5.22 \times 10^5$ cm/sec [49] and the density $\rho = 5.37$ g/cm³.

To illustrate the effect of the non-parabolicity and the $\mathbf{k}$ -dependence of the periodic part of the Bloch functions, we first show in Fig. 1 the sum of the scattering rates due to absorption and emission of polar optical phonons in the (000) valley at 300°K. The dotted curve was calculated from equation (2.10) with $\alpha = 0$ and is therefore appropriate to a parabolic band. The broken curve includes the non-parabolicity of the (000) valley but neglects the $\mathbf{k}$ -dependence of the Bloch functions, while the full curve was calculated directly from equation (2.10). It is seen that while non-parabolicity alone increases the scattering rate, the effect of $\mathbf{k}$ -dependence of the Bloch functions is to again reduce the rate. While the polar scattering rate is a measure of the rate at which an electron loses energy, the angular probability function $P(\cos \beta)$, which is given by equation (3.12) without the angular density of states factor $\sin \beta$, is also needed to assess the rate of loss of momentum. This is shown in Fig. 2 for an electron energy of 0.4 eV and again includes both phonon absorption and emission. It is seen that while non-parabolicity alone emphasizes large angle scattering as compared with the parabolic band result, the $\mathbf{k}$ -dependence of the periodic part of the Bloch functions causes the small angle scattering to be emphasized through the factor $G(\mathbf{k}, \mathbf{k}')$. This behavior is typical of other electron energies although the differences between the various curves in Fig. 2 are smaller at lower energies. Combining the results shown in Figs. 1 and 2, we see that polar scattering will be significantly less effective both in momentum and energy loss when the non-parabolicity and Bloch functions are taken into account at high energy than if non-parabolicity alone is included. Curves like those shown in Figs. 1 and 2 have also been computed using the general expressions given by Kane [27]. These have confirmed that the approximation $\Delta \ll E_g$ makes an insignificant difference to the results.

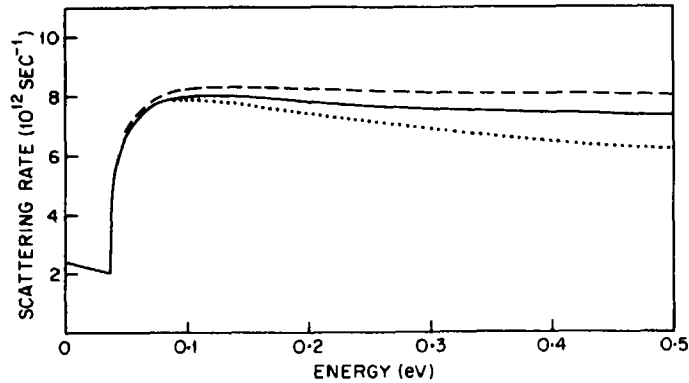


Fig. 1. Energy dependence of the polar scattering rate in the (000) valley of gallium arsenide at 300°K (a) including both the non-parabolicity of the band and the wave vector dependence of the cell-periodic part of the Bloch functions (full curve), (b) including only the non-parabolicity of the band (broken curve) and (c) for a parabolic band (dotted curve).

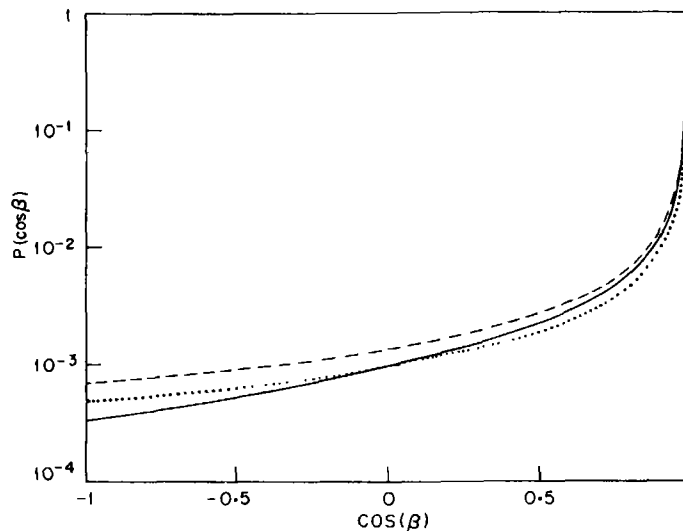


Fig. 2. Angular probability function $P(\cos\beta)$ for an electron energy of 0.4 eV. The labelling of the different curves is the same as in Fig. 1.

The effective mass ratio in the (100) valleys is uncertain, but as discussed in Section 2, this has been taken to be 0.35 and was kept fixed. This is the only parameter in addition to those given above required to calculate the polar scattering rate in the (100) valleys. These values lead to a polar mode limited

mobility in the (100) valleys of about 850 cm^2/Vsec .

Uniaxial stress measurements[33] have given values for the shear and dilatation deformation potentials in the (100) valleys of gallium arsenide. However these values were deduced from changes in the positions of the

(100) valleys with pressure relative to the (000) valley and therefore cannot be used directly in a transport calculation (cf. [14]). In any case these deformation potentials do not appear to be consistent with the results of hydrostatic pressure measurements[35] so we have taken the acoustic deformation potential to be the same as in the (000) valley. This value leads to an acoustic mode limited mobility of about $2000 \text{ cm}^2/\text{Vsec}$ in the (100) valleys.*

If we use silicon as a guide[51], then it is to be expected that scattering between the (100) valleys will be strong. Assuming that the (100) valleys lie at the edge of the Brillouin zone, then transitions between the valleys on different cube axes take place by interaction with the longitudinal optic phonon at the (100) zone edge[52] and this phonon has an angular frequency $\omega_p = 4.54 \times 10^{13} \text{ rad.sec}^{-1}$ [48]. We have taken the deformation potential for this process to be the same as in silicon, $1 \times 10^9 \text{ eV/cm}$ [51] which is also very close to that recently deduced by James[30] from photoemission data.

The combination of these three scattering processes in the (100) valleys leads to a low-field mobility of about $325 \text{ cm}^2/\text{V}^{1/2}\text{sec}^{-1}$. Earlier measurements of the (100) mobility obtained by applying sufficient hydrostatic pressure to depress the (100) valley resulted in values of 150 [53] and 110 [35] $\text{cm}^2/\text{V}^{1/2}\text{sec}^{-1}$. However, recent Hall mobility measurements[36] seem to indicate a much higher value of about $400 \text{ cm}^2/\text{V}^{1/2}\text{sec}^{-1}$ in the better quality epitaxial material. Also, for those materials exhibiting this high mobility, the variation of low-field resistance with pressure is in close agreement with theoretical predictions based on electron transfer to the (100) valleys, whereas for materials with an

apparently lower (100) mobility greater difficulty is experienced in obtaining a fit with the data. Since the calculated value refers to the drift mobility rather than the Hall mobility, the agreement with the experimental value is acceptable.

The only remaining parameter is the intervalley deformation potential Ξ_{ij} required to specify the transition rate between the (000) and (100) valleys. There is little guide as to the correct value to be used in the calculations although James[30] has recently deduced a value of approximately $5 \times 10^8 \text{ eV/cm}$. We therefore present results for values in the range 2×10^8 to $2 \times 10^9 \text{ eV/cm}$.

The variation with energy of the spherically symmetric part of the distribution function is shown in Fig. 3 for various field strengths and for an intervalley deformation potential $\Xi_{ij} = 1 \times 10^9 \text{ eV/cm}$. It is seen that at low field strengths, the distribution is approximately Maxwellian but as the field increases significant structure appears. Below 0.36 eV , the energy separation of the (000) and (100) minima, the 'temperature' of the distribution increases rapidly with field strength, but above this energy the temperature remains close to that of the lattice, the distribution being almost parallel to the zero-field distribution function shown by the broken curve in Fig. 3. This structure in the distribution function can be related to the strength of the various scattering processes as a function of energy. At low energies polar scattering is dominant but the scattering rate, and consequently the rate of loss of electron energy, starts to decrease for this process above about 0.1 eV as was shown in Fig. 1. This results in the distribution becoming very hot between this energy and 0.36 eV . Beyond 0.36 eV however intervalley scattering to the (100) valleys becomes possible and for a deformation potential of $1 \times 10^9 \text{ eV/cm}$ this is dominant resulting in the rapid fall-off in the distribution function. For lower values of the intervalley deformation potential this fall-off is not so rapid as illustrated by Fig. 4. In this diagram

*Since this work was completed, Harris[50] has reported new values for the shear and dilatation deformation potentials. These values lead to an acoustic mode limited mobility of about 50 per cent of that used here but, as we comment in more detail later, this is of little significance to most of the calculated results.

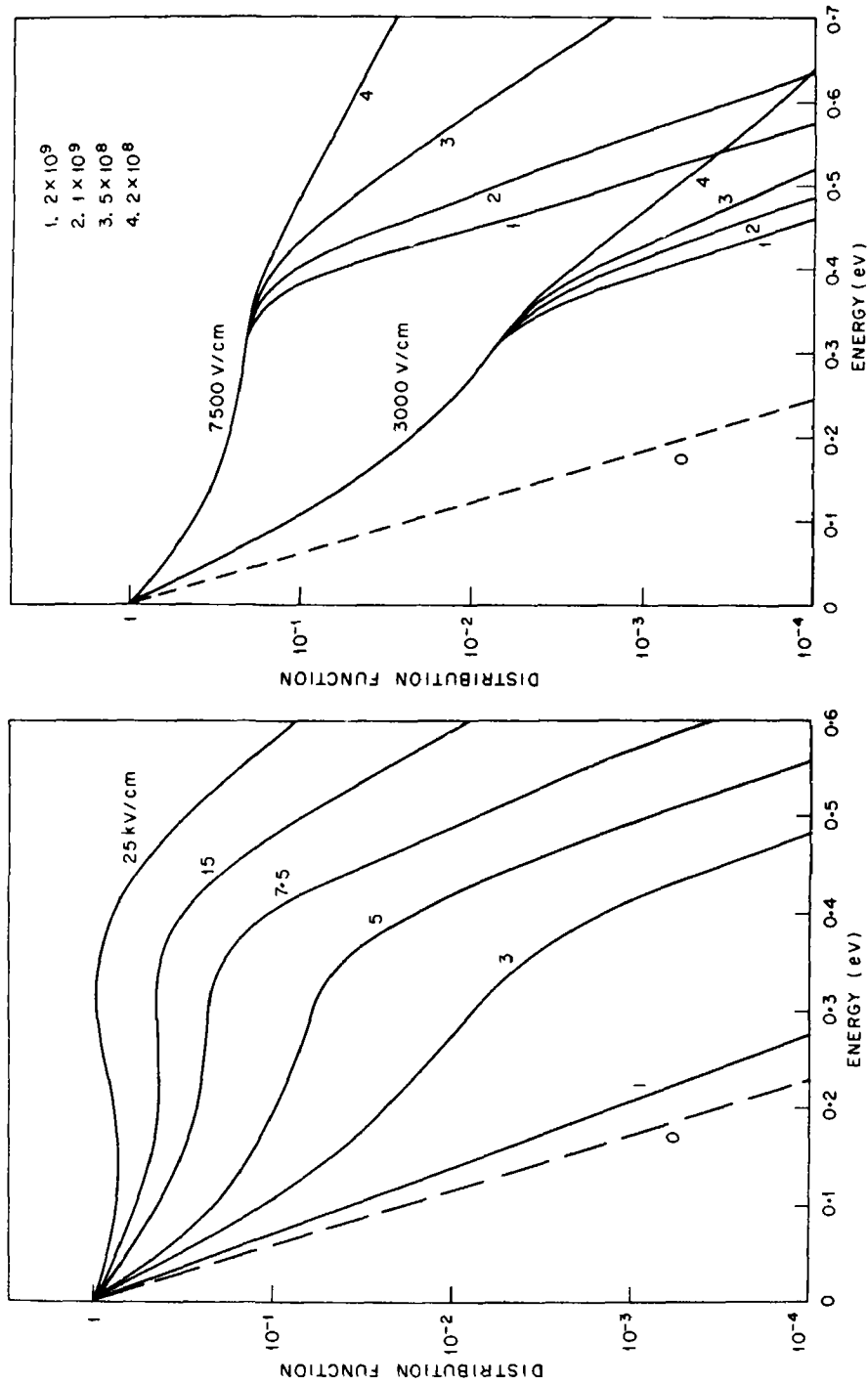


Fig. 3 Energy dependence of the spherically symmetric part of the distribution function in the (000) valley for an intervalley deformation potential of 1×10^9 eV/cm for the field strengths indicated. The broken line is the zero-field Maxwellian

Fig. 4. The effect on the spherically symmetric part of the (000) distribution function at 3000 and 7500 V/cm of varying the intervalley deformation potential over the range 2×10^8 to 2×10^9 eV/cm.

the distribution function at 3000 and 7500 V/cm is shown for intervalley deformation potentials of 0.2, 0.5, 1 and 2×10^9 eV/cm. It is clear that the value of the intervalley deformation potential has a marked effect on the number of carriers with an energy greater than 0.36 eV and hence on the number of carriers in the (100) valleys at a given field strength.

It is noticed in Fig. 3 that the distribution functions at 15 and 25 kV/cm exhibit a population inversion between about 0.2 and 0.36 eV. Figure 5 shows the distribution function in wave-vector space at 15 kV/cm plotted along lines through $\mathbf{k} = 0$ parallel and perpendicular to the electric field, and it is seen that the population inversion is a consequence of a build-up of electrons below 0.36 eV transverse to the field.

As briefly discussed previously[54], this structure in the distribution function in wave-vector space and the resulting population inversion results from the combination of strong momentum randomization above 0.36 eV due to intervalley scattering and the relatively ineffective polar mode scattering below this energy. To see this in more detail, Fig. 6 shows schematically typical trajec-

tories subject to these scattering mechanisms. Electrons with an energy greater than 0.36 eV and with a negative wave-vector component k_z lose energy under the influence of the electric field and enter the region of weak polar scattering. Those electrons with a large wave vector perpendicular to the field, such as those labelled *A* and *B* in Fig. 6, have a high probability of again achieving an energy of 0.36 eV when they will be rapidly scattered to the (100) valleys. On the other hand those electrons with a small value of k_x such as the electron labelled *C* will be scattered by the polar phonons. Consequently the distribution function will be almost constant along lines parallel to the electric field for energies between about 0.2 and 0.36 eV but fall off rapidly at lower and higher energies. This is shown in Fig. 5 for the case of zero k_x .

The build-up of electrons transverse to the field may be understood by noting that electrons such as *A*, *B* and *C* in Fig. 6 exist in this region of momentum-space primarily by being scattered into it from the (100) valleys. Since this process distributes the electrons uniformly over a constant energy surface, the number of electrons entering

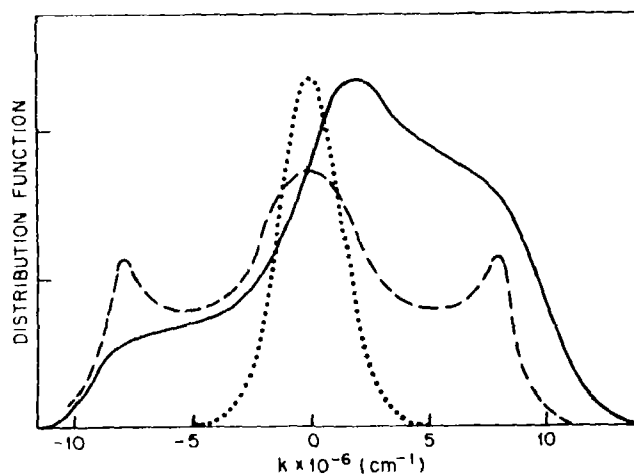


Fig. 5 Plots against $|k|$ of the distribution function in the (000) valley along lines through $\mathbf{k} = 0$ parallel (full curve) and perpendicular (broken curve) to a field of 15 kV/cm. Also included for comparison is the zero-field distribution function (dotted curve).

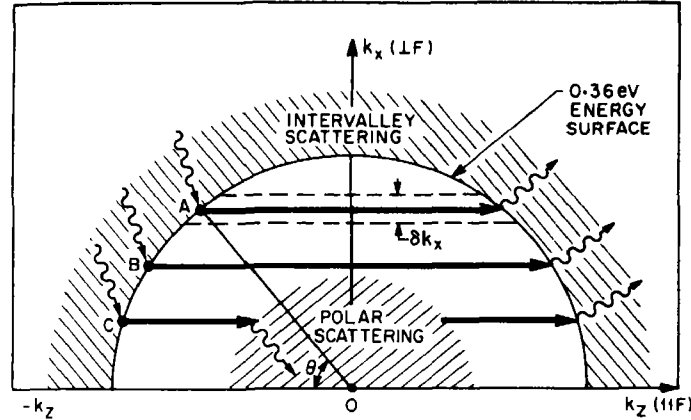


Fig. 6. Schematic representation of electron trajectories in k space giving rise to the population inversion in the (000) valley. See text for discussion.

the region of weak scattering within a fixed interval δk_x increases with k_x in proportion to $1/\cos \theta$. As a result the distribution function also increases with k_x in the range of energies where the scattering is weak, and this is shown in Fig. 5 for the particular case of $k_z = 0$. Also contributing to this transverse inversion is the fact that an electron which is scattered into the (000) valley with an energy somewhat greater than 0.36 eV has a probability which increases with its transverse momentum of reaching 0.36 eV under the influence of the electric field[54]. Similarly, having reached this energy and the region of weak scattering, then the larger the transverse momentum, the shorter is the path length to a particular value of k_z and the less effective is polar scattering along the path due to the higher average electron energies involved.

It is worth noting that the build-up of carriers transverse to the field implies that the second-order coefficient in a spherical harmonic expansion of the distribution function is both large and negative[54]. This is in contrast to the usual behavior at high field strengths, where the representation of the distribution function by only the first two terms in a spherical harmonic expansion is a good approximation because of the high ratio

of thermal to drift velocities. In the calculation by Conwell and Vassell[14] which uses this approximation, no population inversion is therefore predicted.

The population inversion is predicted to exist for field strengths in excess of about 10 kV/cm, although the transverse build-up of carriers becomes evident at lower field strengths. Below about 5 kV/cm the structure in the distribution function becomes less significant and the distribution is quite streamed in the field direction. Characterizing the magnitude of this streaming by the ratio of drift to thermal velocities, it is found that this ratio has a value of about 0.2 at 1 kV/cm and increases to about 0.3 at 2 kV/cm. This value does not then change much up to about 4 kV/cm when it starts to decrease, reaching the value 0.27 at 5 kV/cm and 0.23 at 7.5 kV/cm.

In Fig. 7, the spherically symmetric part of the distribution function in the (100) valleys is shown at various field strengths. It is seen that the scattering is sufficiently strong in these valleys for the distribution to remain Maxwellian up to high field strengths. However this behavior is dependent on the value of the deformation potential coupling the (000) and (100) valleys which in Fig. 7 was taken to be 1×10^9 eV/cm as in Fig. 3.

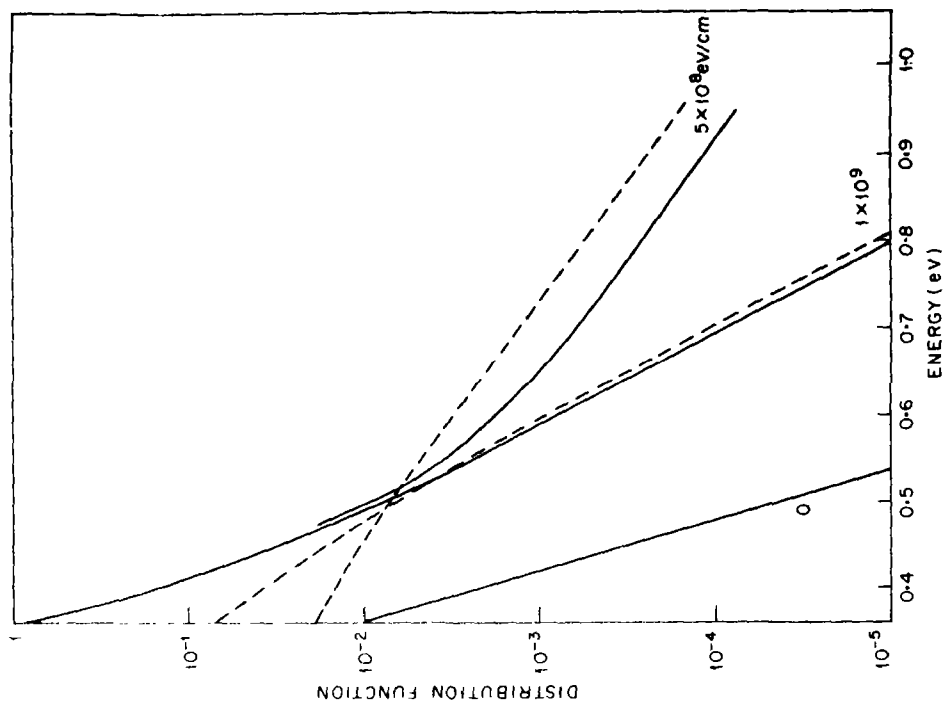


Fig. 8. Comparison of the spherically symmetric part of the distribution functions in the (000) valley above 0.36 eV (broken curves) and in the (100) valley (full curves) at a field strength of 15 kV/cm for intervalley deformation potentials of 1×10^9 and 5×10^8 eV/cm. The energy is measured from the minimum of the (000) valley.

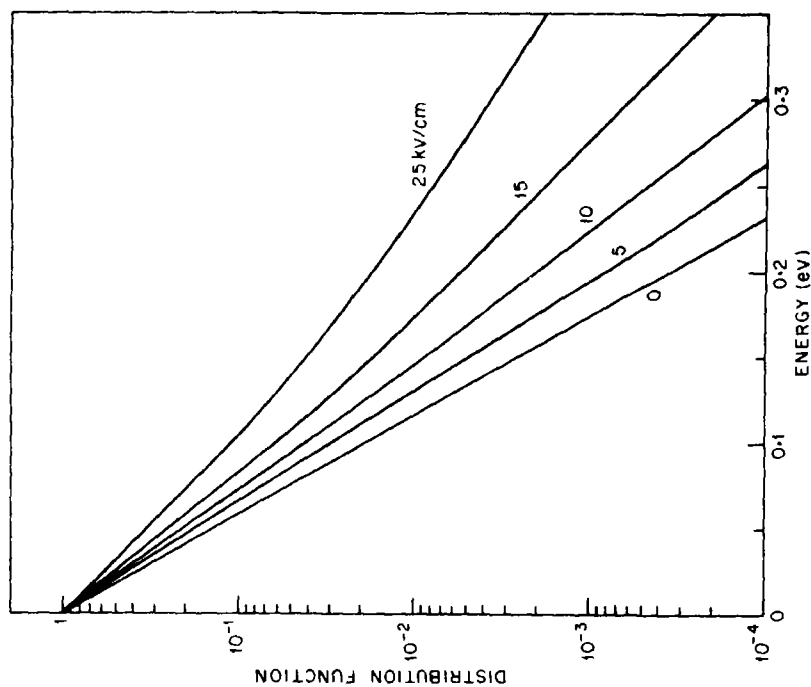


Fig. 7. Energy dependence of the spherically symmetric part of the distribution function in the (100) valley for an intervalley deformation potential of 1×10^9 eV/cm at the field strengths indicated.

In Fig. 8 the (100) distribution function is shown at 15,000 V/cm for intervalley deformation potentials of 1×10^9 and 5×10^8 and compared with the (000) distribution function above 0.36 eV. It is seen that in all cases the (100) distribution is only slightly heated at low energies, as may be seen by comparison with the zero field distribution in Fig. 8. However at high energies the distribution in the (100) valleys follows that in the (000) valley, showing that a substantial part of the electron heating in the (100) valleys arises from the hot electrons in the (000) valley.

In Fig. 9 the average drift velocity is plotted as a function of electric field strength for intervalley deformation potentials Ξ_U of 0.2, 0.5, 1 and 2×10^9 eV/cm. As the strength of the intervalley scattering increases, comparatively fewer carriers have an energy greater than 0.36 eV at a given field strength, as was shown in Fig. 4, and consequently the threshold field for the onset of negative differential mobility and the threshold velocity both increase. Also the magnitude of the maximum negative differential mobility

beyond threshold decreases as Ξ_U is increased. The calculated values for the threshold field, the threshold velocity and the maximum negative mobility are listed in the table.

Intervalley deformation potential (eV/cm)	Threshold field (kV/cm)	Threshold velocity (cm/sec)	Maximum negative mobility (cm^2/Vsec)
2×10^9	2.6	1.70×10^7	5600
5×10^8	3.4	1.96×10^7	3800
1×10^9	3.5	2.02×10^7	2140
2×10^8	3.6	2.06×10^7	1650

The insert in Fig. 9 shows the effect of non-parabolicity and $\mathbf{k}$ -dependent Bloch functions on the drift velocity in the neighborhood of the threshold field for an intervalley deformation of 1×10^9 eV/cm. From Figs. 1 and 2 the effect of non-parabolicity and $\mathbf{k}$ -dependent Bloch functions is to increase the scattering rate compared with that for a parabolic band and this causes the distribution function to be cooler in the (000) valley. As a result the threshold field and velocity are increased

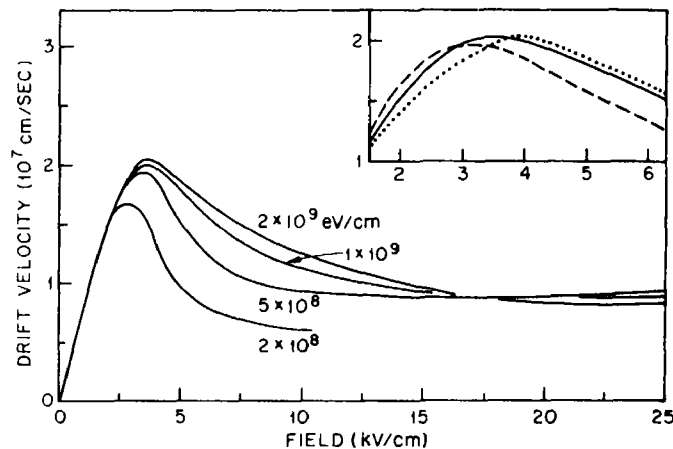


Fig. 9. Electric field dependence of the average drift velocity for intervalley deformation potentials of 0.2, 0.5, 1 and 2×10^9 eV/cm. The inset shows the effect on the drift velocity in the neighborhood of the threshold field of (a) neglecting the wave-vector dependence of the cell-periodic part of the Bloch functions in the (000) valley but retaining the non-parabolicity (dotted curve) and of (b) using a parabolic (000) valley (broken curve) all for an intervalley deformation potential of 1×10^9 eV/cm.

from 3.2 to 3.5 kV/cm and 1.95 to 2.02×10^7 cm/sec respectively. The effect of non-parabolicity alone is to cause a larger increase in these quantities to 4 kV/cm and 2.05×10^7 cm/sec.

Figure 10 shows the variation with field of the electron drift velocity in the (000) valley, and it is seen here that the strength of the intervalley scattering has an even more marked effect than on the average drift velocity. As the value of Ξ_{ij} is increased, the velocity in the (000) valley reduces dramatically for fields in excess of about 3 kV/cm, and for values of Ξ_{ij} of 1 and 2×10^9 eV/cm exhibits a negative differential mobility. This negative differential mobility is about 650 cm²/Vsec for $\Xi_{ij} = 2 \times 10^9$ eV/cm and therefore contributes a significant fraction of the total negative differential mobility. Also shown in Fig. 10 is the drift velocity for an intervalley deformation potential of 1×10^9 eV/cm for a parabolic and non-parabolic (000) valley. For the parabolic valley the drift velocity is significantly higher at the larger field strengths and almost saturates while the

negative differential mobility is increased if non-parabolicity alone is included. The reason that the marked dependence of the (000) valley velocity on the intervalley deformation potential does not show in the average velocity to the same extent may be understood with the aid of Fig. 11, which shows the field dependence of the fraction of electrons in the (100) valleys. It is clear from this diagram that the number of carriers transferred to the (100) valleys decreases as the intervalley deformation potential increases, and so compensates to a large extent for the reduction in the (000) valley velocity. Thus, for example, for deformation potentials of 0.2, 0.5, 1 and 2×10^9 eV/cm the fractions of electrons in the (100) valleys are respectively 0.23, 0.082, 0.046 and 0.032 at 3 kV/cm, 0.67, 0.45, 0.26 and 0.15 at 5 kV/cm and 0.91, 0.74, 0.55 and 0.37 at 10 kV/cm.

If the (000) valley is taken to be parabolic, more electrons are transferred to the (100) valleys at a given field strength and this is shown in Fig. 11 for an intervalley deformation potential of 1×10^9 eV/cm. At 3, 5 and

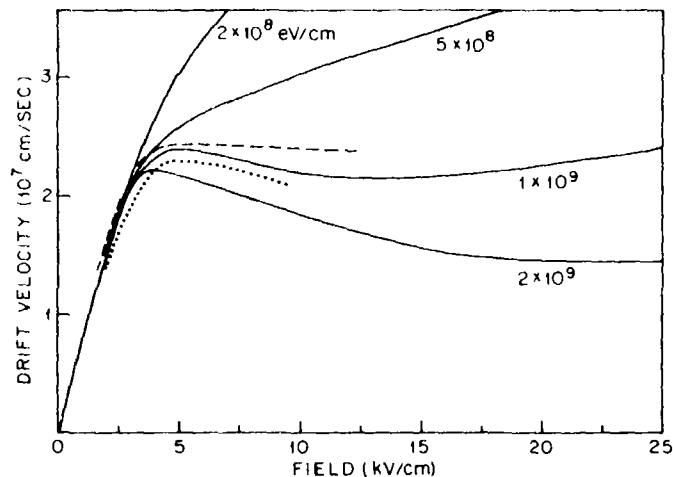


Fig. 10 Drift velocity in the (000) valley as a function of field strength for the intervalley deformation potentials indicated. Also shown is the drift velocity for an intervalley deformation potential of 1×10^9 eV/cm obtained (a) using a parabolic (000) valley (broken curve) and (b) neglecting the wave-vector dependence of the cell-periodic part of the Bloch functions (dotted curve).

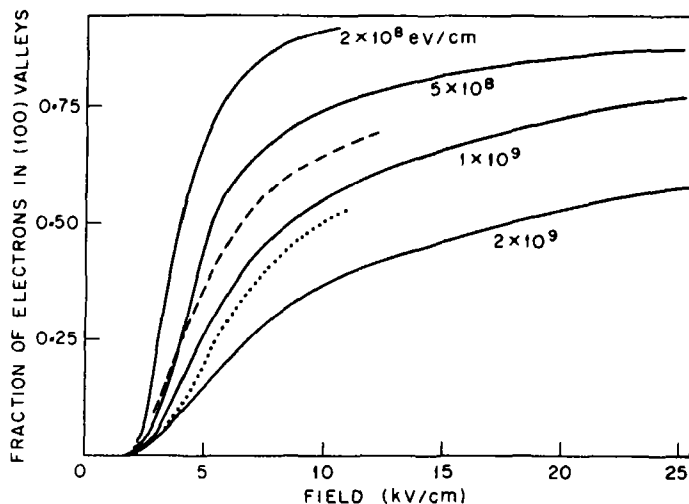


Fig. 11. Fraction of electrons in the (100) valleys for various intervalley deformation potentials. The broken and dotted curves are for an intervalley deformation potential of 1×10^9 eV/cm with respectively a parabolic and non-parabolic (000) valley but neglecting the wave-vector dependence of the cell-periodic part of the Bloch functions.

10 kV/cm the fraction of electrons transferred to the (100) valleys is calculated to be 0.10, 0.38 and 0.65 which are to be compared with the results just given of 0.046, 0.26 and 0.55. If non-parabolicity alone is included, less electrons are transferred, the corresponding numbers being 0.03, 0.19 and 0.50.

Figure 12 shows the calculated mobility in the (000) valley as a function of field again with the intervalley deformation potential as a parameter. It is difficult with the Monte Carlo method to obtain accurate drift velocities at low fields since the contributions from the various parts of the distribution

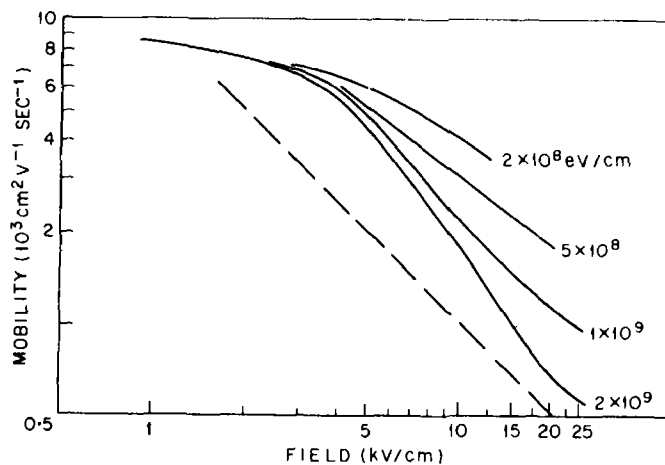


Fig. 12. Field dependence of the mobility of the electrons in the (000) valley for various intervalley deformation potentials. The broken line has a slope of -1 .

cancel to a large extent. Consequently Fig. 12 has not been continued to below 1000 V/cm, but it is still clear that the low-field mobility is calculated to be about $9000 \text{ cm}^2/\text{Vsec}$. Experimental values for the low-field Hall mobility range up to about $10,000 \text{ cm}^2/\text{Vsec}$ in material containing few enough impurities for the mobility to be entirely phonon limited at room temperature. When this value is divided by a factor slightly greater than unity to obtain the drift mobility, and when it is remembered that the material parameters required to calculate the scattering rate are only known to within a few per cent (particularly the dielectric constants which enter as their difference) then the calculated mobility is in satisfactory agreement with experiment. Also a variational calculation of the polar mode limited mobility (Ehrenreich [29]) for parabolic bands leads to a mobility of about $10,000 \text{ cm}^2/\text{Vsec}$ for the parameters used here.

The strong dependence of the (000) velocity on the intervalley deformation potential is again evident in Fig. 12. The broken curve has a slope of -1 and on the log-log plot then represents a mobility proportional to $1/F$; the negative differential mobility in the

(000) valley for intervalley deformation potentials of 1 and $2 \times 10^9 \text{ eV/cm}$ is apparent in this figure through the mobility falling off more steeply than this line.

The mobility in the (100) valleys is also found to be dependent to some extent on the intervalley deformation potential. The calculated mobility in these valleys decreases from its low-field value of $275 \text{ cm}^2/\text{Vsec}$ to 160 at 25 kV/cm for $\Xi_u = 2 \times 10^9 \text{ eV/cm}$ but only to $200 \text{ cm}^2/\text{Vsec}$ for $5 \times 10^8 \text{ eV/cm}$. This low-field value is less than the value of $325 \text{ cm}^2/\text{Vsec}$ quoted above because of intervalley scattering to the (000) valley.

In Fig. 13 the mean energy of the carriers in the (000) and (100) valleys is plotted as a function of electric field strength. In the (000) valley the mean energy is of course not very sensitive to the value of the intervalley deformation potential at low field strengths increasing from 0.039 eV at zero field to about 0.055 eV at 2 kV/cm and to 0.087 eV at 3 kV/cm . Beyond threshold, the mean energy is very dependent on the intervalley deformation potential. For example at 7.5 kV/cm the mean energy is 0.19 eV for a deformation potential of $2 \times 10^9 \text{ eV/cm}$ but 0.27 eV for $2 \times 10^8 \text{ eV/cm}$. The mean energy of the

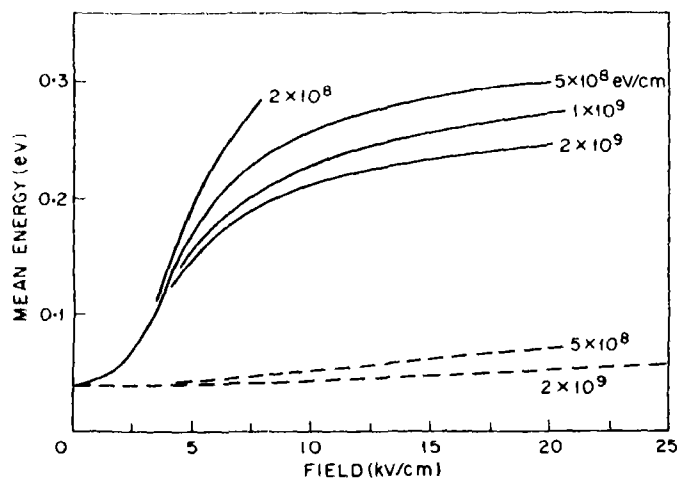


Fig. 13 Mean energy of the electrons in the (000) valley (full curves) and (100) valleys (broken curves) for the intervalley deformation potentials indicated.

electrons in the (100) valleys does not increase very rapidly with field strength as shown in Fig. 13. For an intervalley deformation potential of 2×10^9 eV/cm the mean energy has only increased to about 0.05 eV at 20 kV/cm but is somewhat larger for the smaller deformation potentials.

5. DISCUSSION OF RESULTS

In this section, we first compare the results described in the last section with those of previous calculations[14–16]. The main approximations introduced by Conwell and Vassell[14] were first, that the distribution function in the (000) valley could be represented by the first two terms of a spherical harmonic expansion with respect to energy and second, that the distribution function at an energy ($E \pm \hbar\omega_0$) could be written in terms of the distribution function at E through a Taylor series expansion. As pointed out by Conwell and Vassell, these approximations are only expected to be good when the mean energy is several times the optic phonon energy, and this occurs at a field strength of about 5 kV/cm. However throughout the entire range of field strengths investigated, the form of the distribution function calculated by Conwell and Vassell and its dependence on the intervalley deformation potential is very similar to that calculated here and shown in Figs. 3–8. The only exception to this is the population inversion which, as noted earlier, is not predicted by Conwell and Vassell. Nevertheless the quantitative agreement is poor, not only at low field strengths where some disagreement would be expected, but also at very high field strengths.

A direct quantitative comparison of the results presented in the last section with those calculated by Conwell and Vassell is not possible because of the somewhat different parameters used in this previous work. The most significant difference is in the combined density of states mass in the (100) valleys which in Conwell and Vassell's calculation was taken from Ehrenreich's work[32] to be

$1.2 m_0$, whereas in our case it has the value $0.73 m_0$. This difference would be expected to result in the ratio of the number of carriers in the (100) valleys to the number in the (000) valley being about twice as large in Conwell and Vassell's calculation, but taking account of this still leaves a large discrepancy between the results.

We have therefore used the Monte Carlo method with the same parameters as Conwell and Vassell to calculate the distribution functions in the (000) and (100) valleys using parabolic bands and an intervalley deformation potential of 5×10^8 eV/cm. At 2.5 kV/cm good agreement would not be expected, as mentioned above, and in fact we obtain a mobility in the (000) valley of $7600 \text{ cm}^2/\text{Vsec}$ when the mean energy has increased from 0.039 eV at zero field to 0.072 eV. These values are quite different from those calculated by Conwell and Vassell of about $5200 \text{ cm}^2/\text{Vsec}$ and 0.09 eV. In addition Conwell and Vassell find only about 65 per cent of the electrons remaining in the (000) valley at this field strength as compared with 89 per cent from the Monte Carlo calculation.

At higher field strengths these discrepancies would be expected to disappear to a large extent when the approximations become better. In fact beyond about 5 kV/cm the mean energy and drift velocity in the (000) valley calculated by Conwell and Vassell are very similar to those calculated by the Monte Carlo method. However there is still a large discrepancy between the values calculated for the number of electrons transferred to the (100) valleys. For example at 6 kV/cm Conwell and Vassell find 12 per cent of the electrons remaining in the (000) valley, of which one sixth have energies in excess of 0.36 eV, the remaining 88 per cent being in the (100) valleys. From the Monte Carlo calculation at 6 kV/cm the ratio of the number of electrons above and below 0.36 eV in the (000) valley is one eighth and about 68 per cent are transferred to (100) valleys. The difference in the number of electrons

remaining in the (000) valley, 12 per cent as compared with 32 per cent, has of course a large effect on the average velocity because of the much higher drift velocity in this valley than in the (100) valleys. As a result Conwell and Vassell find an average velocity of 4×10^6 cm/sec at this field strength as compared with about 9×10^6 cm/sec from the Monte Carlo method.

The major part of the discrepancy between Conwell and Vassell's results at high fields and those of the Monte Carlo calculation then appears to arise from the value calculated for the ratio of the number of carriers in the (100) valleys to the number above 0.36 eV in energy in the (000) valley. Denoting this ratio by $\mathcal{R}$ then the numbers just given lead to a value of $\mathcal{R} = 44$ in Conwell and Vassell's calculation but 19 from the Monte Carlo calculation. It is of interest to determine the thermal equilibrium value that $\mathcal{R}$ would have in zero field, and although numerical integration is required, it is straightforward to determine a value of about 15 for a parabolic (000) valley and a (100) density of states mass of $1.2 m_0$. Consequently the small increase in $\mathcal{R}$ found by the Monte Carlo method would imply that the distribution functions in the (100) valleys and in the (000) valley above 0.35 eV were insignificantly heated by the field at 6 kV/cm. This is indeed found to be the case, but since this is also true of the distribution functions calculated by Conwell and Vassell then the high value they find for $\mathcal{R}$ is surprising, particularly since they state that $\mathcal{R}$ does not change much for fields in the range 3 kV/cm to 9 kV/cm.

These ideas are consistent with the values of $\mathcal{R}$ deduced from the distribution functions given in the last section. For the non-parabolic (000) valley considered in the present work and using the (100) effective mass ratio of 0.35, we find the thermal equilibrium value of $\mathcal{R}$ to be 5.25. For the largest intervalley deformation potential considered of 2×10^9 eV/cm, it is then found that $\mathcal{R}$ does not increase noticeably even at the highest field

strengths. However for the smaller intervalley deformation potentials when the distribution function in the (000) valley above 0.36 eV is significantly heated, as demonstrated in Fig. 4, $\mathcal{R}$ does increase with field reaching a value of about 10 at 15 kV/cm for an intervalley deformation potential of 5×10^8 eV/cm, and the same value at about 5 kV/cm for a deformation potential of 2×10^8 eV/cm.

The comparatively large transfer of carriers to the (100) valleys found by Conwell and Vassell results in the average velocity reaching a minimum value beyond threshold at a field strength of about 10 kV/cm at which point the velocity begins to increase significantly. This is to be contrasted with the behavior found here and shown in Fig. 9, where the drift velocity does not reach a minimum value until field strengths in the order of 20–25 kV/cm are reached, when the magnitude of the drift velocity is about twice as large as calculated by Conwell and Vassell due to the larger contribution made by the electrons in the (000) valley. Also, beyond this field strength the drift velocity is found to almost saturate and is not very sensitive to the intervalley deformation potential. This saturation of the drift velocity is of importance in predicting the high electric field strengths measured in propagating domains in the Gunn effect [3, 4].

The displaced Maxwellian approach of Butcher and Fawcett [15, 16] determines the temperature of the distribution and its displacement in momentum space by balancing the average rate of loss of electron energy and momentum due to collisions with that gained from the electric field. This procedure underestimates the number of high energy electrons in the (000) valley, and consequently also underestimates the number of electrons transferred to the (100) valleys. For example at 3 kV/cm using a parabolic (000) valley, Butcher and Fawcett [16] predict 4 per cent of the electrons in the (100) valleys as compared with 20 per cent calculated by the Monte Carlo method using the same parameters. As

a result the drift velocity calculated with displaced Maxwellian distribution functions lies significantly above that found by the Monte Carlo method[22]. In contrast to the discrepancy found in the number of carriers transferred to the (100) valleys, this being sensitive to the form of the high energy tail in the (000) distribution function, the two methods give values for the mean energy and drift velocity in the (000) valley which are in much closer agreement. The only exception to this is at very low field strengths, where the mobility in the (000) valley calculated with displaced Maxwellians is about 20 per cent lower than found by the Monte Carlo method.

We now compare the results described in this section with the available experimental data. There have been many determinations of the velocity-field characteristic in gallium arsenide and diagrams have been published [3, 14] showing the wide spread in the experimental results. Consequently, before a comparison with these results is worthwhile, the techniques used in these measurements have to be examined to try and understand the variation in results and hopefully to select the most reliable measurements.

One of the problems associated with the direct measurement of the drift velocity is that space charge readjustment takes place in the material due to the negative differential mobility. In the first determination of the velocity-field characteristic by Gunn and Elliott[5], an attempt was made to avoid this space-charge accumulation by determining the current through a $10\ \Omega\text{ cm}$ sample using very short 250 psec pulses. The resulting velocity-field characteristic had a negative slope mobility of about $300\text{ cm}^2/\text{Vsec}$ beyond threshold, which was about an order of magnitude lower than theoretical calculations at that time predicted[14, 15] and these calculations were in approximate agreement with deductions from the behavior of lightly-doped gallium arsenide amplifiers[55]. It also appeared to be too low to predict satisfactorily the properties of high field domains characteristic of the Gunn effect.

In more recent work[12] using a refined technique and apparatus with a faster response, it was shown that the above measurement was too slow to avoid space charge effects and this caused the low value of the negative differential mobility. A higher value of about $2000\text{ cm}^2/\text{Vsec}$ is now observed, but it is believed that this technique does not produce an accurate result for the entire velocity-field relationship because of the observed variability in the properties of high resistivity gallium arsenide[56].

The measurements of Braslau[9], Acket[7] and Hamaguchi *et al.*[8] were made by applying a microwave field to the sample. The microwave frequency is then to be chosen high enough to ensure that the field was in the region of negative differential mobility an insufficient time for space charge formation. However, in the measurements made by Hamaguchi *et al.*[8] a microwave frequency of 9.4 GHz and material resistivities of 0.5 and $1\ \Omega\text{ cm}$ were used, and in this case formation of domains would not be prevented. Acket's[7] measurements on the other hand were made with a 35 GHz microwave field and using epitaxial material with resistivities in the range $1\text{--}4\ \Omega\text{ cm}$. The velocity-field curve deduced by Acket shows a threshold which is much higher than determined by any of the other techniques, being about 5 kV/cm ,* and this is also much higher than the threshold measured for Gunn oscillations[3, 4]. Braslau and Hauge[13] have determined the velocity-field relationships for both bulk and epitaxial samples with resistivities in the range $1.5\text{--}20\ \Omega\text{ cm}$ using a 35 GHz microwave field and in Fig. 14 we show the velocity-field relationship for a $1.5\ \Omega\text{ cm}$ epitaxial sample and for a bulk sample of the same resistivity. The

*More recent work by Acket (*Philips Res. Rep.* **23**, 317 (1968); *Phys. Lett.* **29A**, 596 (1969)) have given velocity-field characteristics which are very similar to those shown in Fig. 14. It was also pointed out in the first of these references that in the earlier work[7] the characteristic in the neighborhood of the threshold field had been broadened by material inhomogeneities.

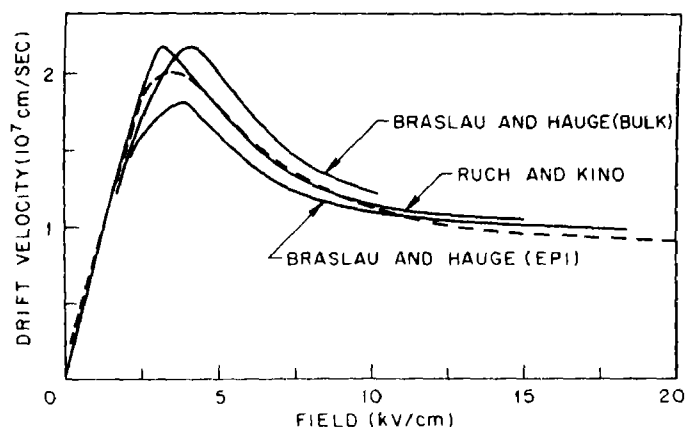


Fig. 14 Experimental velocity-field characteristics determined by Ruch and Kino[11] for insulating gallium arsenide and by Braslau and Hauge[13] for $1.5 \Omega \text{ cm}$ bulk and epitaxial material. Also included for comparison (broken curve) is the drift velocity calculated by the Monte Carlo method for an intervalley deformation potential of $1 \times 10^9 \text{ eV/cm}$

velocity-field relationships of the higher resistivity material in general show a lower negative differential mobility, and in most cases a lower threshold velocity. However the variation in the sample characteristics across the wafer from which they were fabricated indicated that the higher resistivity material was significantly less uniform than the lower resistivity material. This view was supported by the fact that Gunn oscillations in the samples showed a low and variable oscillation amplitude in the higher resistivity material. It should be noted that recent calculations by Rees[21] on the frequency dependence of the electron mobility in gallium arsenide show that at 35 GHz the differential mobility particularly just beyond threshold is somewhat reduced from its d.c. value. However, the velocity field characteristic as deduced from the microwave results will be much less sensitive to frequency since it is deduced from the average conductivity over the microwave cycle.

By measuring the potential distribution in an 82μ long sample which was sufficiently

lightly doped to prevent domain oscillations, Thim[6] has deduced the velocity-field characteristic from Poisson's equation and the current continuity equation. In principle this technique has the advantage that space charge is allowed to form in a well-defined way and the measurements can then be made d.c. However, the drift velocity is a sensitive function of the field gradient in the sample and the lack of resolution of the potential probe and other inaccuracies inherent in this type of measurement only allows the velocity-field curve to be specified within quite wide limits. In fact it has been shown by Kino *et al.*[57] that the velocity-field characteristic measured by Ruch and Kino[11], which is quite different from that deduced by Thim, is consistent with the potential distribution measured in lightly-doped samples.

The measurements of Chang and Moll[10] and Ruch and Kino[11] both employed insulating gallium arsenide with resistivity in the range $10^6 \Omega \text{ cm}$. Consequently oscillations do not occur in this material and electron injection is prevented by a Schottky barrier at

the cathode. The depletion layer in the sample produced by the Schottky barrier under the influence of an applied field produces only an insignificant field gradient in high resistivity material, so that uniform field conditions can be achieved within the sample throughout the whole field range of interest. Electrons are then injected into the sample near the cathode by means of a pulsed gallium arsenide laser[10] or an electron beam[11] and these drift towards the anode under the influence of the applied field. In the Chang and Moll experiment, trapping prevented the electrons from reaching the anode and then the field-dependence of the trapping rate is needed in order to infer the drift velocity from the steady state current, and the scale of the drift velocity remains unknown. On the assumption of a field-independent trapping rate, Chang and Moll deduce a velocity-field characteristic with a threshold field of only 2.2 kV/cm and the velocity reaches a minimum at about 9 kV/cm. However until the exact variation of the trapping rate with electric field is established in such an experiment, no definite conclusion can be drawn, and it should be mentioned that large changes in the deduced velocity-field relationship result for perfectly plausible field dependences of the trapping rate[58]. In the Ruch and Kino experiment trapping of the electrons was so small that the majority of the electrons generated at the cathode reached the anode. Consequently the drift velocity can be deduced directly from the transit time of the electrons through the sample.

In Fig. 14, the velocity-field characteristics measured by Braslau and Hauge[13] and by Ruch and Kino[11] are compared. It is seen that all three curves have almost the same slope in the region of negative differential mobility, but differences exist in the measured magnitudes of the drift velocity. Nevertheless these differences are less than 10 per cent throughout the entire range of field strengths, and this must be regarded as being satisfactory in view of the experimental uncertainties indi-

cated above and the different samples used in the measurements.*

Also included in Fig. 14 is the velocity-field characteristic calculated by the Monte Carlo method for an intervalley deformation potential of 1×10^9 eV/cm. It is seen that the curve is in good agreement with the experiment curves up to the highest field strengths investigated. Unfortunately this good agreement does not allow us to conclude that the intervalley deformation potential is about 1×10^9 eV/cm. The main reason for this is the uncertainty in the effective mass in the (100) valleys and, although the values used in the present work is believed to be reasonable, if subsequent experimental work establishes this mass to have a significantly different value then this would of course change the calculated characteristic. For example an increase in the (100) mass will decrease the threshold field and velocity and increase the negative differential mobility. Since these effects could be balanced to a large extent by an increase in the intervalley deformation potential so retaining the good agreement with experiment, then no definite statement can be made at this stage concerning the exact value of the intervalley deformation potential. Despite this difficulty, it is worth pointing out that the discrepancy between the results described here and those of the approximate treatments[14,16] is so large, being in fact much larger than the changes produced by reasonable variation in the uncertain material parameters, that a deduction of the intervalley deformation potential from these previous results would be completely misleading.

The uncertainty in the mobility in the (100) valleys is by comparison much less significant, at least until very high field strengths because the contribution to the average velocity made by these valleys is quite small. For example

*Recent measurements by Fay and Kino (submitted to *Appl. Phys. Lett.*) of the phase velocity of growing space charge waves propagating in semi-insulating gallium arsenide biased above the threshold field are in excellent agreement with the Ruch and Kino results.

for an intervalley deformation potential of 1×10^9 eV/cm the (100) valleys contribute about 1 per cent of the average velocity at 5 kV/cm, 10 per cent at 10 kV/cm, and 30 per cent at 20 kV/cm. Consequently a large change in the (100) mobility will result in only a small change in the average velocity. Also, at 0.1 eV above the (100) minima, the influence on the average velocity of the (111) minima will be small so long as the electrons in the (000) valley above 0.36 eV and in the (100) valleys are not significantly heated by the electric field, as is the case for an intervalley deformation potential of 1×10^9 eV/cm.

6. CONCLUSION

The principle advantage of the Monte Carlo method of calculating distribution functions and the resulting transport properties is that it gives the exact solution to the Boltzmann transport equation, and this can still be achieved when many scattering processes and complex band structures are necessary. This has been demonstrated here for a two-valley model, one of which is non-parabolic, but the generalization to situations in which more valleys make significant contributions to the average drift velocity is very straightforward since it involves only the addition of extra intervalley scattering processes and corresponding histograms to store the distribution function. This is to be contrasted with the complexity involved in solving a many-valley problem using conventional techniques where it is necessary to solve complicated coupled equations for the distribution function, this being true even for the simplest displaced Maxwellian approach. Thus for example the calculation of high-field transport properties of *n*-type germanium has been carried out using the Monte Carlo method[59] including the ellipsoidal energy surfaces of the (111) and (100) valleys and distinguishing between those (111) or (100) valleys which are not equivalent for a given field orientation. This problem would be prohibitively complex

using analytic approaches even if conventional approximations such as the curtailed spherical harmonic expansion are made. The Monte Carlo method can also be used to determine transport properties in crossed electric and magnetic fields[60] such as the Hall coefficient and magneto-resistance, and is ideally suited to the evaluation of statistical properties such as the diffusion coefficient[61].

In the application of the Monte Carlo method to gallium arsenide described in this paper, the main difficulties lie in the uncertainty in the (100) effective mass and in the (000)–(100) coupling constant, and in the location and influence of the (111) valleys. Despite these difficulties the method gives results which are in good agreement with the best available data provided reasonable values are taken for the uncertain material parameters. It therefore now seems that further progress in the calculation of the high field transport properties of gallium arsenide must await detailed experimental determination of the conduction band structure away from the centre of the Brillouin zone.

Acknowledgements—The authors would like to express their gratitude to I. P. McLean and H. D. Rees for valuable discussions on various aspects of this work. They are also grateful to N. Braslau for communicating results prior to publication. One of us (W.F.) acknowledges the hospitality of the Solid State Device Electronics Department at Bell Telephone Laboratories during the final stages of this work. In particular, thanks are due to J. G. Ruch for assistance in some final computations and to B. J. Roman for discussions. Contributed by permission of the Director of R.R.E. Copyright Controller H.M.S.O.

REFERENCES

1. GUNN J. B., *IBM J. Res. Dev.* **8**, 141 (1964).
2. GUNN J. B., *Solid-State Commun.* **1**, 88 (1963).
3. BUTCHER P. N., *Rep. Prog. Phys.* **30**, 97 (1967).
4. BOTTI L. B. and FAWCETT W., *Adv. Microwaves* **3**, 223 (1968).
5. GUNN J. B. and FLIHOFF B. J., *Phys. Lett.* **22**, 369 (1966).
6. THIM H. W., *Electron. Lett.* **2**, 403 (1966).
7. ACKET G. A., *Phys. Lett.* **24A**, 200 (1967).
8. HAMAGUCHI C., KONO T. and INUISHI Y., *Phys. Lett.* **24A**, 500 (1967).
9. BRASLAU N., *Phys. Lett.* **24A**, 531 (1967).
10. CHANG D. M. and MOLL J. L., *Appl. Phys. Lett.* **9**, 238 (1966).

11. RUCH J. G. and KINO G. S., *Appl. Phys. Lett.* **10**, 40 (1967), also *Phys. Rev.* **174**, 921 (1968).
12. ELLIOTT B. J., *Proc. Inst. Phys. and Physical Soc. and Inst. Elect. Engrs Conf. on Solid St. Devices, Manchester, England* (unpublished) (1967).
13. BRASLAU N. and HAUGE P. S., submitted to *Trans. I.E.E.E. Electron Devices*.
14. CONWELL E. M. and VASSELL M. O., *Phys. Rev.* **166**, 797 (1968) and references to previous work therein.
15. BUTCHER P. N. and FAWCETT W., *Proc. phys. Soc.* **86**, 1205 (1965).
16. BUTCHER P. N. and FAWCETT W., *Phys. Lett.* **21**, 489 (1966).
17. KUROSAWA T., *Proc. Int. Conf. Phys. Semicond., Kyoto, 1966; J. phys. Soc. Japan Suppl.* **21**, 424 (1966).
18. BUDD H., *Proc. Int. Conf. Phys. Semicond., Kyoto, 1966; J. phys. Soc. Japan Suppl.* **21**, 420 (1966).
19. REES H. D., *Phys. Lett.* **26A**, 416 (1968).
20. REES H. D., *J. Phys. Chem. Solids* **30**, 643 (1969).
21. REES H. D., *Solid-State Commun.* **7**, 267 (1969).
22. BOARDMAN A. D., FAWCETT W. and REES H. D., *Solid-State Commun.* **6**, 305 (1968).
23. HILSUM C., *Proc. 7th Int. Conf. Phys. Semicond., Paris* pp. 1127-1139, Dunod, Paris (1964).
24. VREHEN Q. H. F., *Conf. Phys. semicond. Compounds, Swansea, England* (1966).
25. PILLER H., *Proc. Int. Conf. Phys. Semicond., Kyoto, 1966; J. phys. Soc. Japan Suppl.* **21**, 206 (1966).
26. deMEIS W. M. and PAUL W., *Bull. Am. Phys. Soc.* **10**, 344 (1965).
27. KANE E. O., *J. Phys. Chem. Solids* **1**, 249 (1957).
28. HILSUM C., *Prog. Semicond.* **9**, 137 (1965).
29. JAMES I. W., EDEN R. C., MOLL J. L. and SPICER W. E., *Phys. Rev.* **174**, 909 (1968).
30. JAMES I. W., Ph.D. Thesis, Stanford University (1968) (unpublished).
31. SPICER W. F. and EDEN R. C., *Proc. Int. Conf. Phys. Semicond., Moscow*, p. 65 (1968).
32. EHRENREICH H., *Phys. Rev.* **120**, 1951 (1960).
33. SHYAM M., ALLEN J. W. and PEARSON G. L., *Trans. IEEE ED-13*, 63 (1966).
34. BALSLEV I., *Phys. Rev.* **173**, 762 (1968).
35. HUISSON A. R., JAYARAMAN A. and CORIEL L. A. S., *Phys. Rev.* **155**, 786 (1967).
36. PITT G. D. and LEES J., *Proc. Int. Conf. on the Properties of Solids under pressure, CNRS Grenoble Sept 1969*, also submitted to *Phys. Rev.*
37. COHEN M. I. and BERGSTRESSER F. K., *Phys. Rev.* **141**, 789 (1966).
38. JONES D. and LETTINGTON A. H., *Solid State Commun.* **7**, 1319 (1969).
39. POLIAK F. H., HIGGINBOTHAM C. W. and CARDONA M., *Proc. Int. Conf. Phys. Semicond., Kyoto, 1966; J. phys. Soc. Japan Suppl.* **21**, 20 (1966).
40. VAN VECHTEN J. A., *Phys. Rev.* to be published.
41. COLLINS T. C., STUKELI D. J. and EUWEMA R. N., *Phys. Rev.* to be published.
42. HERMAN F., KORTUM R. L., KUGLIN C. D., VANDYKE J. P. and SKILLMAN S., *Methods in Computational Physics* (Edited by B. Adler, S. Fernbach and M. Rotenberg), Vol. 8, Academic Press, New York (1968). See also HERMAN F. and SPICER W. E., *Phys. Rev.* **175**, 906 (1968).
43. OLECHNA D. J. and EHRENREICH H., *J. Phys. Chem. Solids* **23**, 1513 (1962).
44. EHRENREICH H., *J. Phys. Chem. Solids* **2**, 131 (1957).
45. EHRENREICH H., *J. Phys. Chem. Solids* **9**, 129 (1959).
46. MATZ D., *Phys. Rev.* **168**, 843 (1968).
47. PAIGE E. G. S., *Prog. Semicond.* **8**, 62 (1964).
48. WAUGH J. I. F. and DOLLING G., *Phys. Rev.* **132**, 2410 (1963).
49. HAGA E. and KIMURA K., *J. phys. Soc. Japan* **19**, 658 (1964).
50. HARRIS J. S., Ph.D. Thesis, Stanford University (1968) (unpublished).
51. LONG D., *Phys. Rev.* **120**, 2024 (1960).
52. BIRMAN J. I., IAX M. and LOUDON R., *Phys. Rev.* **145**, 620 (1966).
53. WASSE M. P., LEES J. and KING G., *Solid-St. Electron.* **9**, 601 (1966) The value quoted in the text for the (100) mobility is a revised value to that given in this reference.
54. FAWCETT W. and REES H. D., *Phys. Lett.* **28A**, 731 (1969).
55. McWHORTER A. L. and FOYT A. G., *Appl. Phys. Lett.* **9**, 300 (1966).
56. ELLIOTT B. J., IBM Thomas J. Watson Research Center (Private Communication).
57. KINO G. S., ROBSON P. N. and FAY B., *Trans. IEEE Ed-14*, 612 (1967).
58. CHANG D. M. and RUCH J. G., private communication.
59. FAWCETT W. and PAIGE E. G. S., see also Paige E. G. S., IBM J. Res. Dev. **13**, 562 (1969).
60. BOARDMAN A. D. and FAWCETT W., *Phys. Lett.* **29A**, 430 (1969).
61. FAWCETT W. and REES H. D., *Phys. Lett.* **29A**, 578 (1969).

APPENDIX

Proof that the Monte Carlo procedure leads to a distribution function which satisfies the Boltzmann equation

It is straightforward to show that the Monte Carlo procedure outlined in Section 3 leads to a distribution function which satisfies the Boltzmann transport equation. Let us define $P_n(\mathbf{k}_0, \mathbf{k}, t)$ to be the probability that the electron will pass through the state $\mathbf{k}$ at time t during the course of the n 'th free flight in the electric field, having started at the state $\mathbf{k}_0$ at time zero. The explicit time dependence in this definition must be retained since the electron can pass through $\mathbf{k}$ during the n 'th free flight after any time t between 0 and ∞ . The probability function P_n must satisfy the equation

$$\begin{aligned}
 P_n(\mathbf{k}_0, \mathbf{k}, t) = & \int d\mathbf{k}' \int_0^t dt' P_{n-1}(\mathbf{k}_0, \mathbf{k}', t') \\
 & \times \int d\mathbf{k}'' S(\mathbf{k}', \mathbf{k}'') \exp \left[- \int_0^{t-t'} \lambda \left(\mathbf{k}'' + \frac{e\mathbf{F}}{\hbar} \right) dt \right] \\
 & \times \delta \left[\mathbf{k} - \mathbf{k}'' - \frac{e\mathbf{F}}{\hbar} (t - t') \right] \quad (\text{A } 1)
 \end{aligned}$$

The right-hand side of equation (A.1) is the product of three probabilities

(1) the probability $P_{n-1}(\mathbf{k}_0, \mathbf{k}', t')$ that the electron will pass through some state $\mathbf{k}'$ at time $t' \leq t$ during the $(n-1)$ th free flight.

(2) the probability $S(\mathbf{k}', \mathbf{k}'')$ that the electron will be scattered from this state to some other state $\mathbf{k}''$

(3) the probability $\exp\left\{-\int_0^t \lambda\left(\mathbf{k} - \frac{e\mathbf{F}}{h}\mathbf{v}\right) dy\right\}$ that the electron will not be scattered while drifting from $\mathbf{k}''$ to $\mathbf{k}$ during the n th free flight

The delta function ensures that the vector $\mathbf{k} - \mathbf{k}''$ is parallel to the field and has the correct magnitude for the electron to arrive at $\mathbf{k}$ from $\mathbf{k}''$ in the time $(t - t')$. The intermediate states $\mathbf{k}'$ and $\mathbf{k}''$ and the time t' are all integrated over. Using the delta function to do the integration over $\mathbf{k}''$, and making the change of variables to $\tau = t - t'$, $\mathbf{v} = \mathbf{k} - \mathbf{k}'$ we obtain

$$P_n(\mathbf{k}_0, \mathbf{k}, t) = \int d\mathbf{k}' \int_0^t d\tau P_{n-1}(\mathbf{k}_0, \mathbf{k}', t - \tau) \times S\left(\mathbf{k}', \mathbf{k} - \frac{e\mathbf{F}}{h}\tau\right) \exp\left[-\int_0^t \lambda\left(\mathbf{k} - \frac{e\mathbf{F}}{h}\mathbf{v}\right) dy\right] \quad (\text{A.2})$$

If the Monte Carlo calculation proceeds for N collisions, then the count obtained at the state $\mathbf{k}$ is, after normalization,

$$C_N(\mathbf{k}_0, \mathbf{k}) = \frac{1}{N} \lim_{N \rightarrow \infty} \sum_{n=1}^N \frac{1}{T} \int_0^T dt P_n(\mathbf{k}_0, \mathbf{k}, t). \quad (\text{A.3})$$

Substituting for $P_n(\mathbf{k}_0, \mathbf{k}, t)$ from (A.2), and anticipating the form of the Boltzmann equation, by differentiating (A.3), we find that

$$\frac{\partial}{\partial \mathbf{k}} C_N(\mathbf{k}_0, \mathbf{k}) = \frac{1}{N} \lim_{N \rightarrow \infty} \sum_{n=1}^N \frac{1}{T} \int_0^T dt \int d\mathbf{k}' \int_0^t d\tau P_{n-1}(\mathbf{k}_0, \mathbf{k}', t - \tau) \times \frac{\partial}{\partial \mathbf{k}} \left\{ S\left(\mathbf{k}', \mathbf{k} - \frac{e\mathbf{F}}{h}\tau\right) \exp\left[-\int_0^t \lambda\left(\mathbf{k} - \frac{e\mathbf{F}}{h}\mathbf{v}\right) dy\right] \right\} \quad (\text{A.4})$$

Now noting that

$$\frac{\partial}{\partial \mathbf{k}} S\left(\mathbf{k}', \mathbf{k} - \frac{e\mathbf{F}}{h}\tau\right) = -\frac{h}{e\mathbf{F}} \frac{\partial}{\partial \tau} S\left(\mathbf{k}', \mathbf{k} - \frac{e\mathbf{F}}{h}\tau\right)$$

and

$$\frac{\partial}{\partial \mathbf{k}} \exp\left[-\int_0^t \lambda\left(\mathbf{k} - \frac{e\mathbf{F}}{h}\mathbf{v}\right) dy\right] = -\frac{h}{e\mathbf{F}} \frac{\partial}{\partial t} \left[\lambda(\mathbf{k}) \right] \times \exp\left[-\int_0^t \lambda\left(\mathbf{k} - \frac{e\mathbf{F}}{h}\mathbf{v}\right) dy\right]$$

we can rewrite (A.4) as

$$\frac{e\mathbf{F}}{h} \frac{\partial}{\partial \mathbf{k}} C_N(\mathbf{k}_0, \mathbf{k}) = -\lambda(\mathbf{k}) C_N(\mathbf{k}_0, \mathbf{k}) - \lim_{N \rightarrow \infty} \sum_{n=1}^N \frac{1}{T} \int_0^T dt \int d\mathbf{k}' \times \int_0^t d\tau P_{n-1}(\mathbf{k}_0, \mathbf{k}', t - \tau) \times \frac{\partial}{\partial \tau} \left\{ S\left(\mathbf{k}', \mathbf{k} - \frac{e\mathbf{F}}{h}\tau\right) \exp\left[-\int_0^t \lambda\left(\mathbf{k} - \frac{e\mathbf{F}}{h}\mathbf{v}\right) dy\right] \right\}. \quad (\text{A.5})$$

Carrying out the τ integral by parts, and noting that

$$\frac{\partial}{\partial \tau} P_{n-1} = -\frac{\partial}{\partial t} P_{n-1} \text{ we obtain}$$

$$\begin{aligned} \frac{e\mathbf{F}}{h} \frac{\partial}{\partial \mathbf{k}} C_N(\mathbf{k}_0, \mathbf{k}) &= -\lambda(\mathbf{k}) C_N(\mathbf{k}_0, \mathbf{k}) - \lim_{N \rightarrow \infty} \sum_{n=1}^N \frac{1}{T} \int_0^T dt \\ &\times \int d\mathbf{k}' P_{n-1}(\mathbf{k}_0, \mathbf{k}', 0) S\left(\mathbf{k}', \mathbf{k} - \frac{e\mathbf{F}}{h}t\right) \\ &\times \exp\left[-\int_0^t \lambda\left(\mathbf{k} - \frac{e\mathbf{F}}{h}\mathbf{v}\right) dy\right] \\ &+ \lim_{N \rightarrow \infty} \sum_{n=1}^N \frac{1}{T} \int_0^T dt \int d\mathbf{k}' P_{n-1}(\mathbf{k}_0, \mathbf{k}', t) S(\mathbf{k}', \mathbf{k}) \\ &- \lim_{N \rightarrow \infty} \sum_{n=1}^N \frac{1}{T} \int_0^T dt \int d\mathbf{k}' \int_0^t d\tau \\ &\times \frac{\partial}{\partial t} \left\{ P_{n-1}(\mathbf{k}_0, \mathbf{k}', t - \tau) S\left(\mathbf{k}', \mathbf{k} - \frac{e\mathbf{F}}{h}\tau\right) \right. \\ &\times \exp\left[-\int_0^t \lambda\left(\mathbf{k} - \frac{e\mathbf{F}}{h}\mathbf{v}\right) dy\right] \left. \right\}. \quad (\text{A.6}) \end{aligned}$$

Reversing the order of the integration and differentiation in the last term results in two terms, the first of which exactly cancels the second term in equation (A.6), while the second can be written with the aid of (A.2) to be

$$\lim_{N \rightarrow \infty} \sum_{n=1}^N \frac{1}{T} [P_n(\mathbf{k}_0, \mathbf{k}, 0) - P_n(\mathbf{k}_0, \mathbf{k}, T)] \quad (\text{A.7})$$

which is zero. Also the third term can be rewritten from (A.3) in terms of $C_{N-1}(\mathbf{k}_0, \mathbf{k}')$ and we finally obtain

$$\frac{e\mathbf{F}}{h} \frac{\partial}{\partial \mathbf{k}} C_N(\mathbf{k}_0, \mathbf{k}) = -\lambda(\mathbf{k}) C_N(\mathbf{k}_0, \mathbf{k}) + \int d\mathbf{k}' C_{N-1}(\mathbf{k}_0, \mathbf{k}') S(\mathbf{k}', \mathbf{k}). \quad (\text{A.8})$$

In the limit of large N , $C_{N-1} \rightarrow C_N$ and the dependence on $\mathbf{k}_0$ disappears. Equation (A.8) therefore reduces to the Boltzmann equation.

EPR OF Ni^{3+} IN STANNIC OXIDE AND OXIDATION-REDUCTION EFFECTS ON THE EPR SPECTRA OBSERVED IN FLUX-GROWN CRYSTALS

J. A. TUNHEIM*

Physics Department, South Dakota State University, Brookings, South Dakota 57006, U.S.A

and

E. E. KOHNKE, M. D. BELL† and W. J. LEIVO

Physics Department, Oklahoma State University, Stillwater, Okla. 74074, U.S.A

(Received 29 September 1969)

Abstract—EPR spectra of flux-grown stannic oxide single crystals were studied in the X-band at 95 and 300°K. Resonances due to Ni^{3+} as well as to previously reported Fe^{3+} and Cr^{3+} ions were observed. The Nickel center was identified by the diffusion of nickel into vapor-grown crystals. It is found to occupy an interstitial position. The spin Hamiltonian parameters are $s = \frac{1}{2}$, $g_x = 1.96$, $g_y = 6.84$ and $g_z = 5.10$. A superhyperfine structure of approximately 6 G. was also observed. Large differences in signal magnitudes were noted for the above ions in flux-grown crystals in the as-grown, reduced, and oxidized conditions. This is attributed to the loss and gain of oxygen by the crystal and associated changes in ion valency during the heat treatment process. These changes have been used to order several ion ground state energies in relation to the conduction band.

1. INTRODUCTION

ELECTRICAL and optical properties of flux-grown stannic oxide crystals[1] have been under study in our laboratory for some years. Recent photoelectronic measurements[2, 3] have revealed the existence of several electron trapping levels and at least one compensated acceptor sensitizing level in the forbidden bandgap of this material. We have now initiated EPR measurements in an attempt to determine whether the levels observed can be associated with the presence of specific impurities.

Previous EPR studies in stannic oxide have been carried out on vapor-grown specimens. Signals arising from Cr^{3+} [4, 5], Fe^{3+} [6, 7], V^{4+} [8], and Mn^{4+} [9] ions have been reported. In the course of our investigations on flux-grown samples done at both liquid

nitrogen and room temperatures, we have observed four distinct signals. Two of these are due to Cr^{3+} substitutional and interstitial ions as studied by Hou, Summitt, and Tucker in the X-band and in the K and K_1 bands by W. H. From. The third corresponds to the Fe^{3+} signal investigated by Nakada, Ebina and Takahashi and by Sperlich. On the other hand, the fourth signal to our knowledge has not been mentioned in the literature and is here identified as arising from a Ni^{3+} ion in an interstitial site.

The EPR spectra of these ions showed important heat treatment dependences in oxidizing and reducing atmospheres. The effects on the Cr^{3+} ion signals are consistent with those noted by Hou *et al.*, but larger in extent, leading to the conclusion that their proposed mechanism is inadequate to explain our results. The Fe^{3+} signal also shows an extensive heat treatment dependence with lesser effects noted for the Ni^{3+} signal.

The purpose of the present paper, then, is threefold:

*Material presented here has been submitted in partial fulfillment of the requirements for the Ph.D. in physics at Oklahoma State University

†Present address: Physics Department, Central Missouri State College, Warrensburg, Mo. 64093, U.S.A

(1) To report the observation and nature of a new signal, and to identify it as arising from a Ni^{3+} ion in an interstitial site.

(2) To describe the changes noted in nickel, chromium, and iron resonances following heat treatment in oxidizing and reducing atmospheres.

(3) To propose a model which explains these results in terms of the changes in oxygen vacancy concentration resulting from treatment procedures and to give supporting evidence obtained from weight loss measurements.

2. THE NICKEL CENTER

Specimens and EPR experimental procedures

Two types of crystals were used in the study. One series of samples was grown from a cuprous oxide flux in our laboratory. The others were grown from a vapor phase[10] and were made available to us by the Research and Development Laboratory, Corning Glass Works. These latter crystals did not display the unidentified EPR signal of interest in the as-grown condition and were later doped by diffusion of nickel into the sample as discussed below.

The spectrometer employed was a conventional X-band apparatus operating at 9.13 kMc/sec with 100 kc magnetic field modulation. A Varian V-4531 EPR cavity was used with an orientation mount which allowed the rotation of the sample about the vertical axis while at temperatures ranging from -180°C to room temperature. The magnet employed offered a magnetic field range from zero to approximately 4.8 kG.

The crystals were oriented by the Laue back-reflection technique and transferred to the orientation mount. After mounting the orientation of the samples could be further checked to an accuracy of $\pm 0.2^{\circ}$ by use of the Cr^{3+} and Fe^{3+} signals. Magnetic field measurements were obtained with a proton gaussmeter which allowed an accuracy of ± 1 G. All subsequent EPR data were obtained in the same manner.

To test the hypothesis that the previously unreported signal arose from the presence of a nickel center, vapor-grown crystals from Corning Glass—in which the signal was not originally observed—were doped with nickel by a diffusion method similar to that used by Wittke to dope titanium dioxide[11]. A stannic oxide sample was dipped in a methanol–nickel acetate solution and placed in a quartz treatment apparatus. The apparatus was evacuated allowing the methanol to evaporate and the contents were heated to decompose the acetate leaving a nickel oxide residue on the crystal surface. Nitrogen was introduced into the system and the contents were heated to about 1000°C for a period of two weeks. At the conclusion of this treatment, oxygen was admitted into the system and the sample was again heated for 8 hr at the same temperature for the purpose of oxidizing it back to its original stoichiometry.

Subsequent EPR measurements in these treated specimens revealed the appearance of a new signal, due to about 10^{15} centers which corresponded to the flux-grown specimen signal. Similar enhancement of the already present Cr^{3+} signals was observed following an analogous treatment with chromium acetate.

Nickel spectrum results

The nickel center gives a sharp, well-defined signal of linewidth 1–2 G. at both room and liquid nitrogen temperatures. Its orientation dependence is shown in Figs. 1 and 2. Since the nature of the signal indicates a fourfold symmetry exists for the site of this ion, only a 90° interval has been shown. As can be seen, in the (001) plane there are four inequivalent sites which decrease to two in the $[110]$, $[1\bar{1}0]$ and $[100]$ directions.

The rutile-structure site which has this type of symmetry in the undistorted state is an interstitial site[4, 12]. It is surrounded by a distorted octahedron of oxygens of tetragonal symmetry with its tetragonal axis lying $+13^{\circ}$ from the $[110]$ direction. The total symmetry,

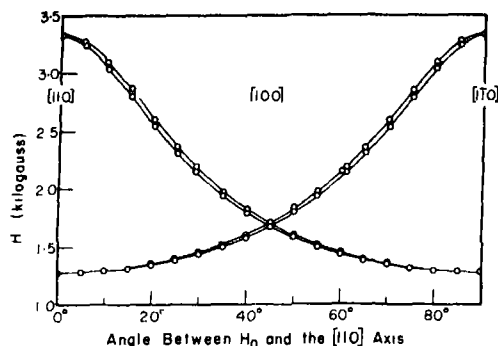


Fig. 1 Observed (circles) and calculated (solid lines) Ni^{3+} resonances in the (001) plane.

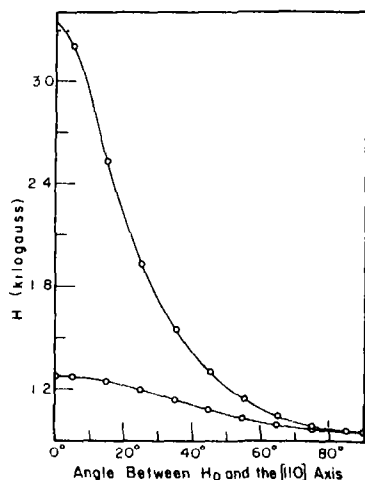


Fig. 2 Observed (circles) and calculated (solid lines) Ni^{3+} resonances in the (110) plane

however, is lowered to C_{2h} by another distorted octahedron of tin atoms of the same symmetry but with its tetragonal axis tilted -45° from the $[110]$ axis. Four inequivalent sites of this type exist, becoming equivalent in pairs in the $[110]$ and $[100]$ directions and all becoming equivalent along the $[001]$ direction. A typical resonance diagram for an ion in such a site will thus have the characteristics of Figs. 1 and 2. Recognizing that both other probable positions for the ion have only two inequivalent sites in the (001) plane [4, 12], we may conclude that the nickel ion

is present in the octahedral coordinated interstitial site. This is not surprising since nickel is also found in the corresponding site in titanium dioxide [12].

The orientation dependence of the nickel signal can be represented by a spin Hamiltonian of effective spin $s = \frac{1}{2}$ and effective g -values $g_x = 1.96$, $g_y = 5.10$ as shown in Figs. 1 and 2 by the solid lines calculated using these parameters where the y -axis is taken along the $[001]$ direction.

On the basis of the $s = \frac{1}{2}$ character of the signal, one expects the valency of the nickel center to be +3 or +1 since these are the only two reasonable valencies of half-integer spin. The trivalent state is to be preferred since both Ni^{3+} and Ni^{2+} are found in titanium dioxide and valencies are for corresponding impurities usually equal or larger in stannic oxide [13–15]. Additional justification for the choice is based on the very large anisotropic g -values which are characteristic of the d^7 system in distorted octahedral coordination [17–19].

The very surprising fact about this system, however, is that the signal is sharp and easily observed at room temperature. Generally the d^7 system can be observed only at temperatures less than 78°K or sometimes even below 20°K . An exception is the Ni^{3+} ion observed in titanium dioxide [12] where it occupies the corresponding interstitial position to that of the Ni^{3+} ions of this study. In the titanium dioxide case, however, the g -values varied only a few tenths from the free spin value due to spin quenching. The reason why the unquenched system of the present study gives rise to a sharp signal at room temperature is unknown to us at this time.

The magnetic x - and z -axes of the crystal do not correspond to the $[110]$ and $[\bar{1}\bar{1}0]$ axes of the crystal, but rather lie $\pm 0.6^\circ$ from these principal directions. One can qualitatively explain this behavior by considering the arrangement of nearest-neighbor oxygen and tin ions. The nearest-neighbor oxygen ions

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form a distorted octahedron with the tetragonal axis in the (001) plane at an angle of 13° from the [110] axis. On the other side of the [110] axis at an angle of 45° in the same plane lies the tetragonal axis of another distorted octahedron formed by the nearest-neighbor tin ions. The magnetic axis may then be expected to lie somewhere between these two directions. Since the nickel-oxygen interaction should be stronger than the nickel-tin interaction, one expects the magnetic axis to be closer to the oxygen tetragonal axis, in agreement with the observed results. Very similar results have been reported for Cr^{3+} in this site with the magnetic axes tilted $\pm 0.5^\circ$ from the [110] axis[4].

In the analogous case of Ni^{3+} in titanium dioxide, the magnetic axis lies at an angle of 9.1° from the [110] direction[12]. One explanation for this difference might be found in the increased covalency of stannic oxide suggested by the larger superhyperfine structure due to neighboring tin ions[5,8]. With a smaller covalent interaction with neighboring metal ions the magnetic axis in titanium dioxide could be expected to lie closer to the tetragonal axis of the nearest-neighbor oxygen ions.

We observed a superhyperfine structure for all orientations other than H_0 parallel to the magnetic c -axis. Although a detailed study of the anisotropy in this structure has not been made, the splitting is approximately 6 G. This is very close to the values reported for the Cr^{3+} interstitial ion[4] and thus the above-mentioned small deviation of 0.1° in the directions of the magnetic axes for these two ions is understandable.

3. HEAT TREATMENT RESULTS

Observed effects on the EPR spectra of flux-grown crystals

Hou, Summitt, and Tucker have observed changes in the EPR spectra of Cr^{3+} ions in vapor-grown stannic oxide crystals after heat treatments in a hydrogen atmosphere.

They have proposed that chromium substitutional ions jump to an interstitial position in the presence of a hydrogen ion. While studying flux-grown crystals, we have observed changes in chromium, iron and nickel signals by utilizing various atmospheres including: air, nitrogen, vacuum, oxygen, helium and hydrogen. Since it was found that large and reproducible changes could be best gotten using oxygen and nitrogen as the treatment ambients, the work reported here will be confined to discussion of heat treatments in these two gases. The observed effects are consistent with those reported by Hou, Summitt, and Tucker although a much greater range of variation was noted.

The basic data upon which the following description is based consist of the EPR spectra of our flux-grown crystals in the highly oxidized, highly reduced, and as-grown conditions. The oxidized condition was obtained by heat treating in an oxygen atmosphere at 900°C for 20 hr and then quenching to room temperature. The reduced condition was obtained with the same treatment using nitrogen instead of oxygen. Supporting data showing consistent trends were also obtained for intermediate states between these extremes. The trends were consistent within the limitations imposed by the difficulty in exactly reproducing the same degree of treatment in different specimens.

The results are as follows:

(1) The Cr^{3+} interstitial ion signal has a maximum amplitude for the reduced condition, becomes quite small in the as-grown condition, and finally disappears in the oxidized condition.

(2) The Cr^{3+} substitutional ion signal is missing for a crystal in the reduced state, reaches a maximum when reduced slightly from the as-grown condition, and decreases to approximately three-fourths its maximum value for the oxidized condition.

(3) The Fe^{3+} ion gives rise to a signal of maximum amplitude when the crystal is in the oxidized state. This signal then becomes

very small for the as-grown crystal and goes to zero for the reduced state.

(4) The EPR signal of Ni^{3+} remains essentially constant except for the reduced state where it decreases slightly.

It is noted here that the dependence of the Cr^{3+} signals reported by Hou, Summitt, and Tucker is consistent with the dependence seen in this study. The greater range observed in this work can be attributed to the lesser amounts of impurities present in our crystals (all four impurities were of concentration less than 1 ppm by wt.) allowing larger Fermi level changes to be induced by the creation of the same number of reduction imperfections. Reinforcing this conclusion is the fact that these vapor-grown crystals changed only slightly in electrical resistance when heat treated in a reducing atmosphere[10] while that of the flux-grown samples decreased by orders of magnitude.

Proposed model for heat treatment effects

The model previously proposed in the literature[4] to explain the heat treatment dependence of Cr^{3+} ion signals is found to be inadequate to explain the data of this study. Proposing that chromium substitutional ions jump to an interstitial position in the presence of a hydrogen ion cannot explain the reversible changes observed for heat treatments in nitrogen and oxygen.

A mechanism which will qualitatively explain both the previously reported data and those of this study can be based upon the assumption that oxygen migrates in and out of the crystal during the treatment processes causing an actual change in stoichiometry. More specifically, oxygen leaves the crystal during the treatment in nitrogen or any other reducing atmosphere, releasing one or two electrons for each atom involved. This raises the Fermi level and may thus cause a change in the valence state of any impurity having a ground state within the range of its rise. As an example, if the Fermi level lies substantially below the Cr^{3+} inter-

stitial ground state most of the interstitial chromium will be Cr^{4+} . This would be the situation for the oxidized condition where no signal is seen arising from the Cr^{3+} interstitial ion. Now, as the crystal is progressively reduced, the Fermi level rises, more Cr^{4+} ions are changed to Cr^{3+} and an EPR signal appears due to the latter ion. Signal changes occur in the reverse order when the reduced sample is oxidized once again. It should be noted here that the integer spin systems such as Cr^{4+} would not be detected for the numbers of centers involved in our crystals.

In search of further support for the proposed model, a series of weight measurements were made to detect the loss of oxygen. A Mettler M5 microbalance with a sensitivity of $\pm 2 \mu\text{g}$ was used. A large number of crystals of approximately 1.2 g combined weight were placed in a small quartz capsule and weighings were made of both the capsule and the crystals. A weight loss of about 6 parts in 10^5 (by wt.) was observed for samples heat treated in nitrogen for twenty hours at 900°C after a similar treatment in oxygen. After again treating in oxygen the weight lost was reversibly regained.

Similar consideration applied to the iron and nickel ions suggest a method for ordering their ground state energies in the forbidden gap. On the basis of the proposed model and the heat treatment dependence of the EPR spectra a schematic diagram is given in Fig. 3 for the ion ground state energies in relation to the conduction band. The reasoning

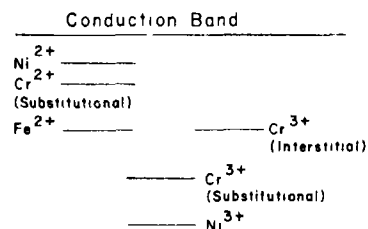


Fig. 3 Indicated relative order of several ion ground state energies below the conduction band.

involved in the level placement is as follows: the Cr^{2+} substitutional ground state is placed close to the conduction band since the Cr^{3+} substitutional signal vanishes only for a very highly reduced state of the crystal. Since the Fe^{3+} signal is small for the as-grown state of the crystal, the Fe^{2+} levels are partially occupied. Also the Cr^{3+} interstitial signal is quite small in the as-grown state, thus both the Fe^{2+} and Cr^{3+} interstitial ground states probably lie in the region of the Fermi level in the as-grown crystal. Substitutional Cr^{3+} signals decrease only for the very highly oxidized condition and its ground state has been placed lower in the forbidden gap, possibly 1 eV or more below the conduction band. Since the Ni^{3+} signal decreases only slightly for the reduced state, its ground state is even lower with the Ni^{2+} state very close to the conduction band.

It must be emphasized again that only the ordering of the levels should be considered significant. Actual energy values await correlation with other experimental data.

Acknowledgements—The authors wish to thank the National Aeronautics and Space Administration for the financial support provided for this work under NASA Grant NSG-609. The research program of which this is a part received its initial support from the Office of Naval Research under Contract No. Nonr-2595(01). Special thanks are due to the Research and Development

Laboratory, Corning Glass Works and Dr. R. W. Summitt for furnishing us with several vapor-grown specimens used in the study.

REFERENCES

1. KUNKLE H. F. and KOHNKE E. E., *J. appl. Phys.*, **36**, 1489 (1965).
2. HOUSTON J. E. and KOHNKE E. E., *J. appl. Phys.*, **36**, 3931 (1965).
3. HOUSTON J. E. and KOHNKE E. E., *J. appl. Phys.*, **37**, 3083 (1966).
4. HOUS L., SUMMITT R. W. and TUCKER R. F., *Phys. Rev.*, **154**, 258 (1967).
5. FROM W. H., *Phys. Rev.*, **131**, 961 (1963).
6. NAKADA R. E., FBINA A. and TAKAHASHI T., *J. phys. Soc. Japan*, **21**, 188 (1966).
7. SPERLICH G., *Z. Naturf.*, **23a**, 1967 (1968).
8. KIKUCHI C., CHEN W., FROM W. H. and DORAIN P. B., *J. chem. Phys.*, **42**, 181 (1965).
9. FROM W. H., DORAIN P. B. and KIKUCHI C., *Phys. Rev.*, **135**, A710 (1964).
10. MARLEY T. A. and MACAVOY T. C., *J. appl. Phys.*, **32**, 2504 (1961).
11. WITTKI J. P., *J. electrochem. Soc.*, **113**, 193 (1966).
12. GERRITSEN H. J. and SABISKY E. S., *Phys. Rev.*, **125**, 1853 (1962).
13. ANDERSEN H. G., *J. chem. Phys.*, **35**, 1090 (1961).
14. GERRITSEN H. J., HARRISON S. E., LEWIS H. R. and WITTKI J. P., *Phys. Rev. Lett.*, **2**, 153 (1959).
15. GERRITSEN H. J. and LEWIS H. R., *Phys. Rev.*, **119**, 1010 (1960).
16. GERRITSEN H. J. and SABISKY E. S., *Phys. Rev.*, **132**, 1507 (1963).
17. GLADNEY H. M., *Phys. Rev.*, **143**, 198 (1966).
18. YAHNAKA F. and BARNES R. G., *Phys. Rev.*, **125**, 1568 (1962).
19. FINKHAM M., *Proc. R. Soc. Lond.*, **A238**, 549 (1956).

THE TEMPERATURE DEPENDENCE OF THE PLANAR HALL EFFECT IN IRON, COBALT AND NICKEL*

M. L. YU† and J. T. H. CHANG

Physics Department, University of Hong Kong, Hong Kong

(Received 15 September 1969)

Abstract—The temperature dependence of the Spontaneous Planar Hall Effect in the ferromagnetic metals: iron, cobalt and nickel has been studied. Measurements were made from room temperature to the Curie point in case of nickel and up to 600°C in case of iron and cobalt. The following empirical relationships among the planar Hall coefficient P_s , magnetization M and the resistivity ρ were established: $P_s \sim M^2(M_0^2 - M^2)$ with different values of M_0 for iron and nickel, and $P_s \sim M^2(\alpha\rho + \beta\rho^2)$ for cobalt. For cobalt, different pairs of (α, β) were found for the hcp (low temperature) and the fcc (high temperature) structures. Temperature hysteresis was observed in the region of phase transformation. Possible resemblances with the usual Spontaneous Hall Effect were investigated.

1. INTRODUCTION

THE PLANAR Hall Effect[1] arises when a current is allowed to flow through a conductor placed in a magnetic field. An electric field is developed in the plane formed by the current vector and the magnetic field vector and is perpendicular to the current direction. This planar Hall field is a sine function of the angle ' θ ' between the magnetic field H and the current density j . It is given by

$$E_p = jP_0H^2 \sin\theta \cos\theta \quad (1)$$

where P_0 is the planar Hall coefficient. Jan[2] found that this 'pseudo-Hall effect' is actually a consequence of magnetoresistance. Phenomenologically, it can be shown that the product

$$P_0H^2 = \rho_{\parallel} - \rho_{\perp} \quad (2)$$

where $\rho_{\parallel}$ is the resistivity in a longitudinal magnetic field and $\rho_{\perp}$ is the resistivity in a

transverse magnetic field. In nonmagnetic metals, this difference is often too small that their planar Hall effect attracted little attention. However in 1966 Vu Dinh Ky[3] reported that in nickel the spontaneous magnetization M brought the planar Hall voltage to a level comparable to the usual Hall effect. In his phenomenological theory [4], he established that the spontaneous planar Hall field

$$E_p = jP_sM^2 \sin\theta \cos\theta \quad (3)$$

where P_s is the spontaneous planar Hall coefficient. In case of nickel[3] he found that $P_s \sim 7 \times 10^{-13} \text{ V-cm/A-G}^2$. Again

$$P_sM^2 = \rho_{\parallel} - \rho_{\perp} = \Delta\rho_s \quad (4)$$

and the last quantity is often defined as the ferromagnetic resistivity anisotropy [2].

2. EXPERIMENT

The measurement of the planar Hall voltage is similar to the usual Hall effect except that the sample is now placed with its plane parallel to the magnetic field. As in usual Hall effect measurements, an alternating current technique was employed to eliminate

*Based on a thesis submitted by the first author to the Physics Department, University of Hong Kong, 1969 in partial fulfillment of the requirements for the degree of Master of Science.

†Now at Physics Department, California Institute of Technology, Pasadena, Calif. 91109, U.S.A.

all the interfering d.c. voltages such as thermoelectric potentials[5]. Nernst and Ettingshausen effects however were negligible with such a geometry. The usual threeprobe balance method[6] was used to minimize the misalignment voltage developed across the Hall probes. Besides, with this arrangement, the thermal stability requirement and magnetoresistance effects affecting the misalignment voltage would not enter[7]. Usual Hall voltages came up from the fact that the sample might not be perfectly parallel to the magnetic field. This was eliminated with the field reversal technique as it is an odd function of the magnetic field. The major difficulty in the use of the a.c. technique was the induced e.m.f. within the Hall voltage detection loop when the sample vibrated in the applied magnetic field[8]. This was improved by pressing the samples hard onto the sample holder and by aligning carefully the current and voltage leads, minimizing the area of the loops formed. Besides, as the planar Hall voltage is an odd function of ' θ ' this spurious e.m.f. was eliminated by taking the mean of two readings, one with angle ' θ ' and the other with ' $-\theta$ '. However, with well aligned samples, this voltage was often less than 1 per cent of the planar Hall voltage.

A power amplifier provided the one ampere sample current. 175 Hz was chosen as it was midway between the second and third harmonics of the line frequency. A PAR HR-8 phase sensitive Lock-In Amplifier equipped with a low input impedance pre-amplifier was used to measure the planar Hall voltage with $\pm 0.01 \mu\text{V}$ accuracy. A Varian V-4005 4-in. electromagnet provided the uniform magnetic field. As the demagnetization factor was small with such a geometry, a maximum field of 12 kG was enough in all cases.

For room temperature measurements of which the angular dependence was desired, the metal samples in form of a thin rectangular plate were fixed on a modified spectrometer

table. For high temperature measurements, the samples were fixed in a microfurnace the oxygen within which was removed with magnesium ribbon. Direct current heating was used to prevent vibration of the furnace within the magnetic field and also to minimize excessive line voltage pick up. All current and voltage leads were platinum wires spot welded onto the metal samples. Experiment with nickel had been performed from room temperature to the Curie point while measurements on cobalt and iron were made up to 600 and 550°C respectively.

The samples each of 0.005 in. thick were supplied by the ALFA Inorganic Company with purity 99.998%, 99.7% and 99.998% for iron, cobalt and nickel respectively. Samples were annealed at 600°C for 15 hr. However practically no change in planar Hall voltage was detected within experimental error for samples with and without heat treatment. This was consistent with the remark made by Jan[2] on ferromagnetic resistivity anisotropy.

3. RESULTS AND DISCUSSIONS

Figure 1 shows the angular dependence of the spontaneous Hall fields normalized to unit current density for the three ferromagnetic metals. The sinusoidal variation is as predicted. At room temperature the planar Hall coefficient of nickel is about $7.8 \times 10^{-13} \text{ V-cm/A-G}^2$ which is quite close with that reported by Vu Dinh Ky[3]. That for cobalt is $6.8 \times 10^{-14} \text{ V-cm/A-G}^2$ and $0.95 \times 10^{-14} \text{ V-cm/A-G}^2$ for iron. The planar Hall voltages were practically constant after saturation (Fig. 2) showing that the contribution from the magnetizing field itself was negligible. The spontaneous planar Hall voltage was taken by extrapolating the high field readings to $H = 0$ assuming a quadratic field dependence.

The temperature variation of the planar Hall coefficient of iron and nickel is shown in Figs. 3. and 4. For both metals, P_x increases with temperature and the maximum value

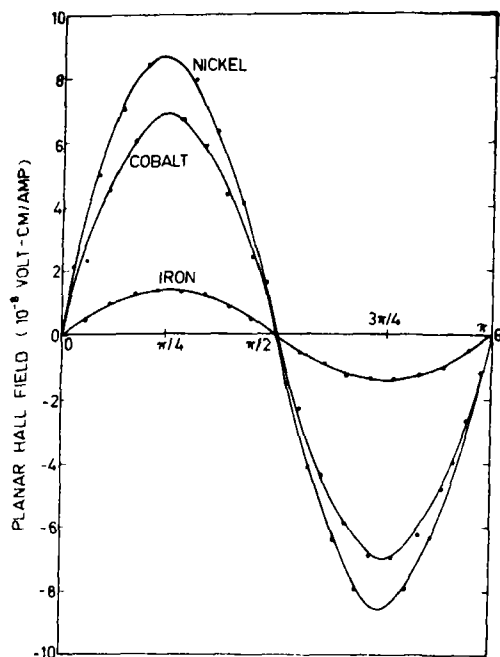


Fig. 1 The angular dependence of the spontaneous Hall fields at unit current density.

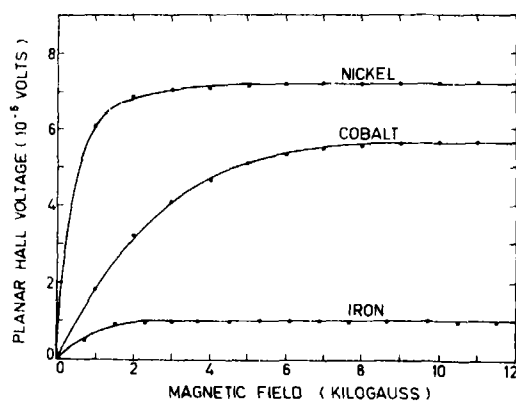


Fig. 2 The field dependence of the planar Hall voltages at room temperature. Current = 1 A, thickness = 0.005 in, $\theta = 45^\circ$

was reached in the case of nickel and dropped rapidly as the Curie point was approached. We tried to relate P_s with the spontaneous magnetization M . An empirical relationship

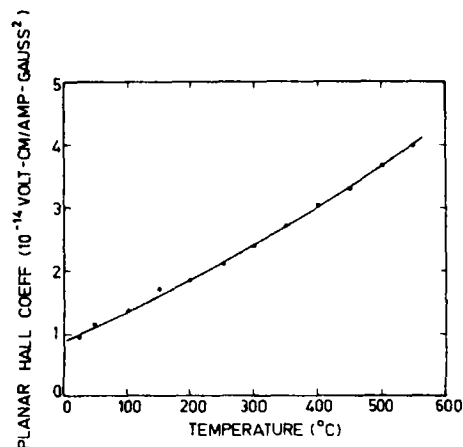


Fig. 3 The temperature dependence of the spontaneous planar Hall coefficient of iron.

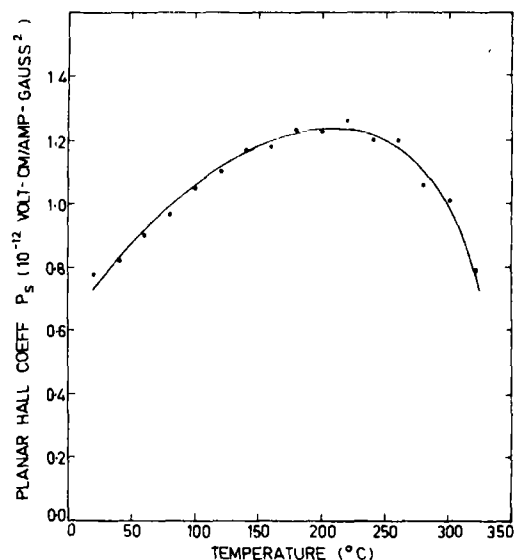
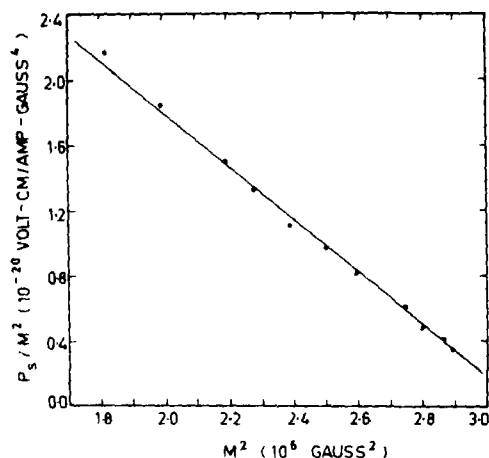
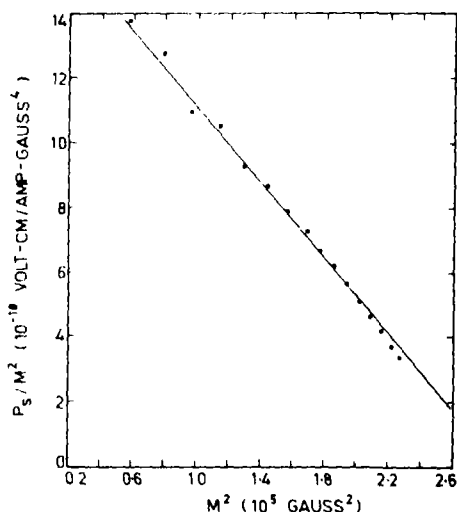


Fig. 4. The temperature dependence of the spontaneous planar Hall coefficient of nickel.

was found:

$$P_s \sim M^2(M_0^2 - M^2). \quad (5)$$

This is illustrated by the straight lines obtained when P_s/M^2 is plotted against M^2 in Figs. 5 and 6. Here the constants M_0 have the same

Fig. 5 Dependence of P_s/M^2 on M^2 for iron.Fig. 6 Dependence of P_s/M^2 on M^2 for nickel.

dimension as M and were found to be 3.9 and 5.9 per cent higher than the spontaneous magnetization at absolute zero for iron and nickel respectively.

It is of interest to note that the functional form in equation (5) is not unique among galvanomagnetic effects of ferromagnetics. The usual spontaneous Hall coefficient R_s does obey similar relationships. For example $R_s \sim \text{const.}^2 - M^2$ for nickel[9]. From

Lavine's data for Grade A nickel[10] we found that the constant is approximately 1.6 per cent higher than the spontaneous magnetization at absolute zero. Actually such a result was predicted theoretically when a $4s$ orbit- $3d$ spin interaction together with spin-disorder scattering are considered [11, 12].

The pattern of the temperature variation of the planar Hall effect in cobalt differs from the other two. The effect of the ϵ - γ phase transformation around 425°C is particularly marked. Cobalt has a fcc structure (γ -phase) above 450°C and the hcp structure (ϵ -phase) is the stable form at lower temperatures. The transition is actually gradual and exhibits an hysteresis. It was reported by Bogma and Zubove[13] that both the phase transformation and its hysteresis were reflected in the Hall effect and other galvanomagnetic properties. This was also true for our planar Hall effect measurements. However when the sample was taken in succession through repeated cycles, the path followed was not constant but it seemed to depend upon the former thermal history of the metal. A measurement of the resistivity indicated that the temperature interval involved was large, roughly from 225 to 525°C although the major change was around 375 – 475°C . One such cycle is shown in Fig. 7.

Although the planar Hall effect is very structural sensitive, there is practically no jump in saturation magnetization at the phase transition. The simple form $M^2(M_0^2 - M^2)$ for P_s failed to fit our experimental results for cobalt. Even the usual spontaneous Hall effect of cobalt is very structural sensitive and does not obey $R_s \sim \text{const.}^2 - M^2$. It was reported that R_s was related more directly to the resistivity ρ . Actually it was found that

$$R_s = a\rho + b\rho^2 \quad [14] \quad (6)$$

where different pairs of (a, b) are assigned to the two different phases. This is consistent with spin-orbit interaction theories for the

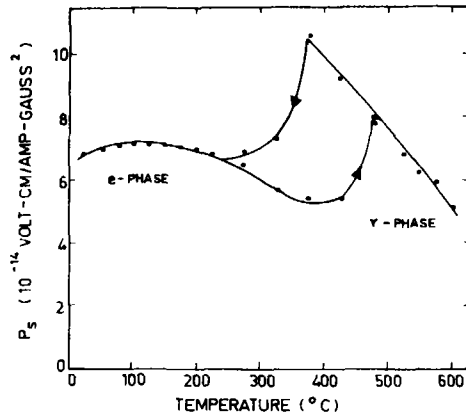


Fig. 7. The temperature dependence of the spontaneous planar Hall coefficient of cobalt, indicating the temperature hysteresis.

spontaneous Hall effect when impurity and phonon scattering are considered as the chief conduction mechanisms:

$$R_s = a\rho + b\rho^2 \text{ for impurity scattering [15].}$$

$$R_s = c\rho^2 \text{ for phonon scattering [16].}$$

Recalling that in the case of nickel, the quantity P_s/M^2 is similar in behaviour to R_s , we suspected that this quantity for cobalt might be related to the resistivity in a similar manner. A plot of $P_s/\rho M^2$ against ρ in Fig. 8 showed it is actually the case, though a slight curvature exists in the region of phase transformation. The low and high temperature portions obey the linear relationship more closely. Thus

$$P_s \sim M^2(\alpha\rho + \beta\rho^2) \quad (7)$$

and again different pairs of (α, β) are assigned to the two different phases.

It seems very probable that both the spontaneous Hall and planar Hall effects may be explained under the same scheme. However one point of interest is that for iron $R_s \sim \rho^2$ while P_s contains the factor $(M_0^2 - M^2)$ instead. Actually even before Vu Dinh Ky introduced the idea of treating the problem as a planar Hall effect, many workers ap-

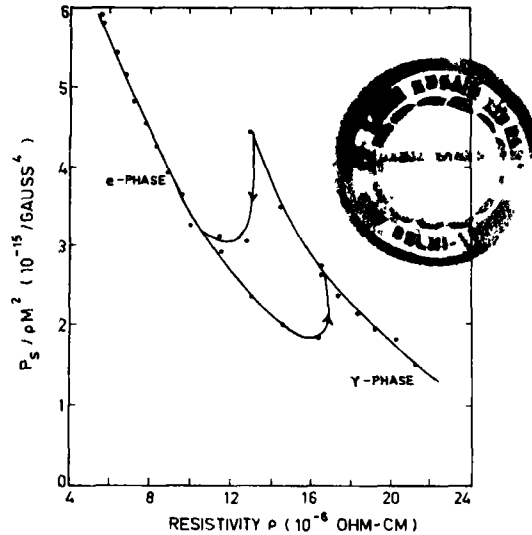


Fig. 8. Dependence of $P_s/\rho M^2$ on ρ for cobalt, indicating the hysteresis.

proached it through the consideration of resistivity anisotropy. Many theoretical attempts were already made along the line of considering $4s-3d$ exchange interaction and various types of spin-orbit interaction [17-20]. Actually Berger[21] applied the same spin-orbit interaction scheme to explain both the usual spontaneous Hall effect and the resistivity anisotropy of ferromagnetic alloys. However it seems all the theoretical efforts made up to the present failed to predict the empirical relations obtained in our experiment in contrast to the success obtained in case of the usual spontaneous Hall effect.

The extra ' M^2 ' factor appearing in our empirical formulae for P_s might suggest that the planar Hall effect is actually a fourth order effect. We recall that in Vu Dinh Ky's phenomenological theory, he expanded the resistivity tensor element ρ_{yx} in powers of M_x, M_y . There the current density j was along the x -axis and the planar Hall field E_y was along the y -axis while the magnetization M was on the x - y plane. By taking the second order approximation and inserting symmetry requirements he arrived at this equation:

$$E_p = jP_s M_x M_y \\ = jP_s M^2 \sin\theta \cos\theta. \quad (8)$$

Suppose we take also the third order terms $M_x^3, M_x^2 M_y, M_x M_y^2, M_y^3$ and fourth order terms $M_x^4, M_x^3 M_y, M_x^2 M_y^2, M_x M_y^3, M_y^4$. Using the fact that $\rho_{yx} = -\rho_{xy}$, only $M_x^3 M_y$ and $M_x M_y^3$ remain. Applying Onsager's symmetry requirement that $\rho_{yx}(M_x, M_y) = \rho_{xy}(-M_x, -M_y)$ we see that they should have the same coefficient in the expansion. Thus

$$E_p = j\rho_{yx} \\ = j[bM_x M_y + c(M_x^3 M_y + M_x M_y^3)] \\ = j(b + cM^2)M^2 \sin\theta \cos\theta. \quad (9)$$

Hence

$$P_s = b + cM^2.$$

That our results favour a ' M^2 ' factor in P_s suggested that either (1) b implicitly contains the factor ' M^2 ', (2) the main contribution is from the fourth order term cM^2 .

A simple experiment was performed to distinguish this two cases. The sample was

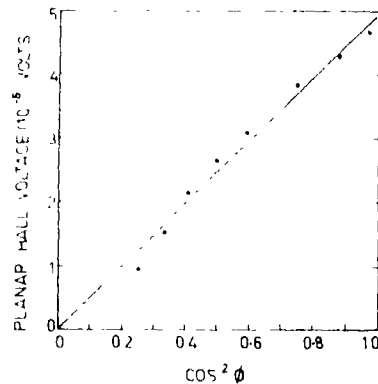


Fig. 9 Dependence of the spontaneous planar Hall voltage of nickel at room temperature on angle ϕ

deliberately placed in such a way that the magnetizing field made an angle ϕ with the x - y plane. Thus the factor M in former derivations has to be replaced by $M \cos\phi$. So E_p should depend upon $\cos^2\phi$ in the first case, and $\cos^4\phi$ in the second case. Results shown on Fig. 9 supports the first assumption.

Acknowledgements—We wish to express our sincere gratitude to Professor A. J. Lyon for his continual support on the research, Dr. R. M. Yu for his valuable suggestions, and to Mr. K. I. Yau for his pioneer work on the planar Hall effect in permalloys. Financial support and the award of a Studentship to the first author from the Committee on Higher Degree and Research Grants of the University of Hong Kong are gratefully acknowledged.

REFERENCES

1. GOLDBERG C. and DAVIS R. E., *Phys. Rev.* **94**, 1121 (1954).
2. JAN J. P., *Solid St. Phys.* **5**, 1 (1955).
3. VU DINH KY, *Soviet Phys. JETP* **23**, 809 (1966).
4. VU DINH KY, *AN SSR ser. Fiz.* **29**, 576 (1965), transl. *Bull. Acad. Sci. Phys. Ser.* p. 581.
5. DONOGHUE J. J. and EATHERLY W. P., *Rev. scient. Instrum.* **22**, 513 (1951).
6. SCHINDLER A. I. and PUGH F. M., *Phys. Rev.* **89**, 295 (1953).
7. YU M. L., Thesis, University of Hong Kong, July (1969) (unpublished).
8. GUTHRIE G. L., *Rev. scient. Instrum.* **36**, 1177 (1965).
9. KIKON I. K. and IGOSHEVA I. N., *Soviet Phys. JETP* **19**, 48 (1964).
10. LAVINE J. M., *Craft Lab., Harvard University, Tech. Rep.* No. 225, March 10 (1956) (unpublished).
11. IRKHIN Yu. P. and ABEL'SKII Sh. Sh., *Soviet Phys. solid St.* **6**, 1283 (1964).
12. KAGAN Yu. and MAKSIMOV L. A., *Soviet Phys. solid St.* **7**, 422 (1965).
13. BOGMA K. K. and ZUBOV V. V., *Physics Metals Metallogr.* **19**, 288 (1964).
14. CHREMUSHKINA A. V. and VASIL'EVAR P., *Soviet Phys. solid St.* **8**, 659 (1966).
15. LUTTINGER J. M., *Phys. Rev.* **112**, 729 (1958).
16. IRKHIN Yu. P. and SHAVROV G. V., *Soviet Phys. JETP* **15**, 754 (1962).
17. SMIT I., *Physica* **16**, 612 (1951).
18. KONDO J., *Prog. theor. Phys.* **27**, 772 (1962).
19. VU DINH KY, *Soviet Phys. JETP* **24**, 995 (1967).
20. PETROVA L. N., *Soviet Phys. solid St.* **10**, 8 (1968).
21. BERGER I., *Physica* **30**, 1141 (1964).

ON THE FOURTH-ORDER ANHARMONIC EQUATION OF STATE OF SOLIDS*

LEON THOMSEN

Lamont-Doherty Geological Observatory of Columbia University, Palisades, N.Y. 10964, U.S.A.

(Received 21 April 1969, in revised form 8 September 1969)

Abstract—The non-uniqueness of the definition of finite 'strain' is demonstrated to lead to significant ambiguities in the equation of state of elastic solids. The ambiguities are resolved by the rigorous derivation (due to Leibfried and Ludwig) of the Mie-Grüneisen equation. Closed expressions for $\phi_0(V)$ and $\gamma(V)$ are presented which contain *no* assumptions additional to those already present in the simple M-G equation. Numerical equations of state for NaCl and MgO are presented which satisfy all ultrasonic and shock-compression data. Comparison with previous tabulations for NaCl reveals small but significant discrepancies.

1. FINITE STRAIN

It is a well-known result[1, 2] of continuum mechanics that the theory of finite strain may be written equivalently in terms of any of an infinite number of different definitions of the 'strain'. For the case of an *elastic* solid (i.e. one possessing a free-energy function which is uniquely defined in terms of deformation and temperature), this result implies, specifically, that the *stress-strain relation* may be written equivalently in an infinite number of ways.

As examples, if the strain $\mathbf{e}$ is defined implicitly in terms of the deformation $\mathbf{R}-\mathbf{R}_0$ by

$$\mathbf{R}-\mathbf{R}_0 = \mathbf{e}\mathbf{R}_0 \quad (1)$$

then the stress-strain relation is

$$\boldsymbol{\sigma} = (\mathbf{I} + \mathbf{e}) \left(\frac{\partial F}{\partial \boldsymbol{\eta}} \right)_T (\mathbf{I} + \mathbf{e}^\dagger) \frac{1}{V}. \quad (2)$$

Here $\mathbf{R}$ is a vector to a point in the deformed lattice, $\mathbf{R}_0$ is the vector to the same point in the undeformed reference state, denoted in this section by a sub-zero. The components of both are referred to the same set of

Cartesian axes. $\mathbf{e}$ is the finite strain tensor defined by (1). $\boldsymbol{\sigma}$ is the (homogeneous) stress at the point $\mathbf{R}$. $\mathbf{I}$ is the unit 3×3 tensor, $(\mathbf{I})_{ij} = \delta_{ij}$. F is the Helmholtz free energy, or 'elastic energy' function. $\boldsymbol{\eta}$ is the symmetric finite strain tensor defined in relation to $\mathbf{e}$ by

$$\eta_{ij} \equiv \frac{1}{2}(e_{ij} + e_{ji} + e_{mj}e_{mi}). \quad (3)$$

Equation (2) is exact, i.e. independent of the size of $\mathbf{e}$. It is derived by, e.g. Leibfried and Ludwig[3] and by Murnaghan[4].

Alternatively, the strain $\mathbf{f}$ can be defined implicitly by

$$\mathbf{R}-\mathbf{R}_0 = \mathbf{f}\mathbf{R} \quad (4)$$

and then the stress-strain relation is

$$\boldsymbol{\sigma} = (\mathbf{I} - 2\boldsymbol{\epsilon}) \left(\frac{\partial F}{\partial \boldsymbol{\epsilon}} \right)_T \frac{1}{V} \quad (5)$$

with the symmetric tensor $\boldsymbol{\epsilon}$ defined in relation to $\mathbf{f}$ by

$$\epsilon_{ij} \equiv \frac{1}{2}(f_{ij} + f_{ji} - f_{mj}f_{mi}). \quad (6)$$

Equation (5) is also exact, though its generality is restricted to special situations, including the important cases of isotropic bodies, and of

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pure strains unaccompanied by rotations. It is derived by, e.g. Murnaghan[5].

Not directly involved in the proofs of (2) and (5) are the relations between strain and volume change:

$$\left(\frac{V}{V_0}\right)^2 = |\det(\mathbf{I} + 2\boldsymbol{\eta})| \quad (7)$$

$$\left(\frac{V_0}{V}\right)^2 = |\det(\mathbf{I} - 2\boldsymbol{\epsilon})| \quad (8)$$

V is, of course, specific volume.

The difference between these two definitions of strain (1) and (4) is clearly in the choice of the characteristic lengths used as coefficients of the strain on the RHS of the two definitions. In the first case, the characteristic lengths are taken from the reference state; in the second, from the deformed state. Because of this essential difference, the strains $\boldsymbol{\epsilon}$ and $\boldsymbol{\eta}$ are called *Lagrangian* or *material* definitions of strain; the strains $\mathbf{f}$ and $\boldsymbol{\epsilon}$ are called *Eulerian* or *spatial*. These, and other definitions of strain can be, and have been, derived with more generality than is needed here. An elegant, and exhaustive, discussion of finite strain is given by Truesdell[1]; a more limited, pedagogic treatment is given by Thomsen[6].

Although (2) and (5) are exact, their usefulness is limited by the need for expressions for the free energy as a function of the strain. In general, the physical description of the free energy in terms of interatomic forces, etc. will impose requirements on the choice of a definition of strain[7]. Also, any approximations made in F will affect the results of the choice of a definition of strain. Hence, the application of (2) and (5) to real solids will not be exact, and further, will depend critically upon the choice of a definition of strain. Different choices lead to non-equivalent equations of state

As an illustration of this, consider the special case of hydrostatic pressure P on an isotropic body. Both (2) and (5) reduce to

$$P = -\left(\frac{\partial F}{\partial V}\right). \quad (9)$$

Equations (7) and (8), however, do *not* reduce to the same form, but rather to

$$\eta = \frac{1}{2} \left[\left(\frac{V}{V_0} \right)^{2/3} - 1 \right] \quad (7a)$$

$$\epsilon = -\frac{1}{2} \left[\left(\frac{V_0}{V} \right)^{2/3} - 1 \right] \quad (8a)$$

$$= \left(\frac{V_0}{V} \right)^{2/3} \eta. \quad (8b)$$

The fact that V_0 appears in the denominator of (7a) and in the numerator of (8a) is an expression of the essential difference between the Lagrangian and the Eulerian definitions of strain.

If the free energy is assumed to be of the form

$$F = \sum_{i=1}^{i_m} A_i \eta^i \quad (10)$$

with $i_m = 3$, then (9) and (7a) give the *third-order Lagrangian isotherm*

$$P = \frac{2}{3} K_0 (y^{1/3} - y^{-1/3}) [1 - \frac{2}{3} K'_0 (y^{-2/3} - 1)] \quad (11)$$

where y is the volume ratio

$$y = \frac{V_0}{V} = \frac{\rho}{\rho_0}. \quad (12)$$

Here the coefficients A_i have been evaluated in terms of the boundary value measurements at the reference state, taken here to be defined by $P = 0$, $T = T_0 =$ room temperature. K is the isothermal incompressibility; K' is $(\partial K / \partial P)_T$; ρ is density. This equation appears in Murnaghan's 1951 monograph[4], p. 71.

As is clear from the symmetry apparent in (2) and (5), or in (9), (7a) and (8a), an assumption equally as plausible (at this point in the argument) as (10) is

$$F = \sum_{j=1}^{j_m} B_j \epsilon^j \quad (13)$$

with $j_m = 3$. Equations (9) and (8a) then lead to the *third-order Eulerian isotherm*

$$P = \frac{3}{2} K_0 (y^{7/3} - y^{5/3}) (1 + \frac{3}{4} (K'_0 - 4) (y^{2/3} - 1)). \quad (14)$$

This equation has achieved prominence in the literature as the Birch-Murnaghan (B-M) equation of state through its application by Birch[8-11] and others to problems of finite compression in the interior of the earth. It was apparently first written by Murnaghan[5] in an early exposition of the thoughts which led eventually to his 1951 treatise.

The difference between (11) and (14) is an increasing function of y , becoming serious for $y \gtrsim 1.2$. The divergence is illustrated in Fig. 1, where curves for (11) and (14) are shown, together with the Lagrangian and Eulerian fourth-order isotherms corresponding to $i_m = 4$, in (10) and to $j_m = 4$ in (13), respectively. Also shown for comparison is a curve of the Murnaghan equation (12)

$$P = \frac{K_0}{K'_0} (y^\beta - 1) \quad (15)$$

where $\beta = K'_0$.

The fourth-order curves require a knowledge of $K''_0 = (\partial^2 K / \partial P^2) T_0|_{P=0}$, which is not measurable directly. Later sections of this paper develop a way of determining this quantity indirectly. Figure 1 is drawn for a material with properties similar to NaCl. Since the *fourth-order Lagrangian isotherm* is considered the most important, Fig. 1(b) shows the deviations of the others from this.

The main point of Fig. 1 is to demonstrate that the ambiguity mentioned above is real, and serious for large compressions. The ambiguity is not resolvable with concepts of continuum mechanics, but requires a physical description of F in terms of an atomistic theory.

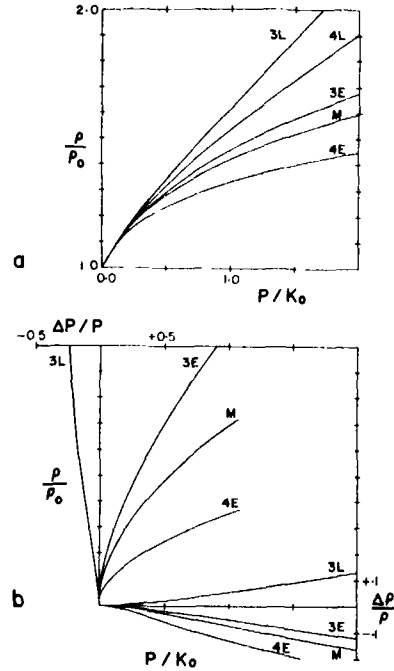


Fig. 1 (a) The upper set of curves is isothermal equations of state for third (3L) and fourth (4L) order Lagrangian formulas, for third (3E) and fourth (4E) order Eulerian formulas, and for the Murnaghan formula (M). (b) The lower two sets of curves describe the (percentage) departures of 3L, 3E, 4E, and M from 4L, in two ways: (1) as pressure differences at constant density, as functions of density (vertical scale), and (2) as density differences at constant pressure, as functions of pressure (horizontal scale).

2. LATTICE DYNAMICS—THE POTENTIAL ENERGY

As Knopoff has pointed out[7], each model of atomic interaction leads to a definition of strain appropriate to that model, and thence to an equation of state appropriate to that model. The purpose of this paper is to identify the definition of finite strain appropriate to that model of atomic interaction which underlies the theory of lattice dynamics, and to examine the consequences that follow. Only centrosymmetric lattices are considered. The model is defined by the assumption that the instantaneous lattice potential energy at time t may be approximated by a Taylor expansion in the atomic displacements:

$$\begin{aligned}
\Phi(l) = & \phi_0(\cdots \mathbf{R} \cdots) + \sum_i \phi_{\mu}^m q_{\mu}^m \\
& + \frac{1}{2} \sum_{ij} \phi_{\mu\nu}^{mn} q_{\mu}^m q_{\nu}^n \\
& + \frac{1}{3!} \sum_{ijk} \phi_{\mu\nu\kappa}^{mnp} q_{\mu}^m q_{\nu}^n q_{\kappa}^p \\
& + \frac{1}{4!} \sum_{ijkl} \phi_{\mu\nu\kappa\lambda}^{mnpq} q_{\mu}^m q_{\nu}^n q_{\kappa}^p q_{\lambda}^q + \cdots \quad (16)
\end{aligned}$$

The notation here is that of Leibfried and Ludwig[3]; in fact, it is fairly said that most of the ideas presented here are implicit, and some are explicit, in that excellent review. Briefly q_{μ}^m is the i component of the displacement from equilibrium of the μ th atom in the unit cell which is located by $\mathbf{m}$. The Coupling Parameter of first order, ϕ_{μ}^m is the indicated partial derivative of Φ , evaluated at the equilibrium configuration $(\cdots \mathbf{R} \cdots)$ and so is a function of volume. The sums (over repeated indices) cover all lattice sites. The termination of the expansion at the fourth order is important, when thermal effects are significant, for reasons that appear presently.

It is desired to express (16) in terms of an expansion about a *fixed* reference position. The assumption of (16) as written requires, for example, that the first term be expandable as

$$\begin{aligned}
\phi_0(\cdots \mathbf{R} \cdots) = & \tilde{\phi}_0(\cdots \tilde{\mathbf{R}} \cdots) \\
& + \sum_i \tilde{\phi}_{\mu}^m (R_{\mu}^m - \tilde{R}_{\mu}^m) \\
& + \frac{1}{2} \sum_{ij} \tilde{\phi}_{\mu\nu}^{mn} (R_{\mu}^m - \tilde{R}_{\mu}^m)(R_{\nu}^n - \tilde{R}_{\nu}^n) \\
& + \frac{1}{3!} \sum_{ijk} \tilde{\phi}_{\mu\nu\kappa}^{mnp} (R_{\mu}^m - \tilde{R}_{\mu}^m)(R_{\nu}^n - \tilde{R}_{\nu}^n)(R_{\kappa}^p - \tilde{R}_{\kappa}^p) \\
& + \frac{1}{4!} \sum_{ijkl} \tilde{\phi}_{\mu\nu\kappa\lambda}^{mnpq} (R_{\mu}^m - \tilde{R}_{\mu}^m) \\
& \times (R_{\nu}^n - \tilde{R}_{\nu}^n)(R_{\kappa}^p - \tilde{R}_{\kappa}^p)(R_{\lambda}^q - \tilde{R}_{\lambda}^q) + \cdots \quad (17)
\end{aligned}$$

where the super-tilde denotes evaluation in the fixed reference state. The reference state may be chosen arbitrarily, so long as the approximation implied by the truncation in (16) and (17) is not violated. It is convenient here to choose that state as the one where ϕ_0 is at a minimum (hence $\tilde{\phi}_{\mu}^m = 0$). This configuration, $(\cdots \tilde{\mathbf{R}} \cdots)$, of course would be that assumed by the crystal if it were harmonic. That it is not realized in an actual crystal except under unusual circumstances is of no concern here. It will be referred to as the 'rest' state. The coefficients $\tilde{\phi}_{\mu\nu}^{mn}$ etc., are, of course, constants.

The *strain* is introduced here for the first time as a simplifying notation. Using the simple Lagrangian definition (1),

$$R_{\mu}^m - \tilde{R}_{\mu}^m = e_{\mu\mu}^{mm} \tilde{R}_{\mu}^m \quad (18)$$

and assuming the strain to be homogeneous throughout the crystal, ϕ_0 is

$$\begin{aligned}
\phi_0(\cdots \mathbf{R} \cdots) = & \tilde{\phi}_0(\cdots \tilde{\mathbf{R}} \cdots) \\
& + \frac{1}{2} \sum_{ij} \tilde{\phi}_{\mu\nu}^{mn} R_{\mu}^m R_{\nu}^n e_{ij} e_{ij} \\
& + \frac{1}{3!} \sum_{ijk} \tilde{\phi}_{\mu\nu\kappa}^{mnp} R_{\mu}^m R_{\nu}^n R_{\kappa}^p e_{ir} e_{js} e_{kt} + \frac{1}{4!} \sum_{ijkl} \tilde{\phi}_{\mu\nu\kappa\lambda}^{mnpq} \\
& \times R_{\mu}^m R_{\nu}^n R_{\kappa}^p R_{\lambda}^q e_{ir} e_{js} e_{kt} e_{lu} + \cdots \quad (19)
\end{aligned}$$

The other terms of (16) are also expandable in this way, but they do not appear in the equation of state, and so are not treated here.

It is a simple matter to convert the expansion (19) in $\mathbf{e}$ to the equivalent expansion in $\boldsymbol{\eta}$ appropriate to the stress-strain relation (2) and the rotational invariance of ϕ_0

$$\begin{aligned}
\phi_0 = & \tilde{\phi}_0 + \frac{1}{2} \tilde{V} \sum \tilde{c}_{ijkl} \eta_{ij} \eta_{kl} \\
& + \frac{1}{3!} \tilde{V} \sum \tilde{c}_{ijklmn} \eta_{ij} \eta_{kl} \eta_{mn} \\
& + \frac{1}{4!} \tilde{V} \sum \tilde{c}_{ijklmnop} \eta_{ij} \eta_{kl} \eta_{mn} \eta_{pq} \quad (20)
\end{aligned}$$

where

$$\bar{c}_{ijkl} \equiv \frac{1}{\bar{V}} \left. \frac{\partial^2 \phi_0}{\partial \eta_{ij} \partial \eta_{kl}} \right|_0 \quad (21a)$$

$$\bar{c}_{ijklmn} \equiv \frac{1}{\bar{V}} \left. \frac{\partial^3 \phi_0}{\partial \eta_{ij} \partial \eta_{kl} \partial \eta_{mn}} \right|_0 \quad (21b)$$

$$\bar{c}_{ijklmnop} \equiv \frac{1}{\bar{V}} \left. \frac{\partial^4 \phi_0}{\partial \eta_{ij} \partial \eta_{kl} \partial \eta_{mn} \partial \eta_{pq}} \right|_0 \quad (21c)$$

Though the description of the $\bar{c}_{ijkl}$ in terms of the $\bar{\phi}_{\mu\nu}^{\mu\nu} \bar{R}_{\mu}^{\mu} \bar{R}_{\nu}^{\nu}$ is easy [3, 6], it is not given here. Again, the $\bar{c}_{ijkl}$ etc., are constants.

Turning now to the Eulerian definition of strain, it is clear that an equally valid representation of the static potential energy is:

$$\begin{aligned} \phi_0 = & \bar{\phi}_0 + \frac{1}{2} \sum_{ij} \bar{\phi}_{\mu\nu}^{\mu\nu} R_{\mu}^{\mu} R_{\nu}^{\nu} f_{ir} f_{js} \\ & + \frac{1}{3!} \sum_{ijk} \bar{\phi}_{\mu\nu\kappa}^{\mu\nu\kappa} R_{\mu}^{\mu} R_{\nu}^{\nu} R_{\kappa}^{\kappa} f_{ir} f_{js} f_{kt} \\ & + \frac{1}{4!} \sum_{ijkl} \bar{\phi}_{\mu\nu\kappa\lambda}^{\mu\nu\kappa\lambda} R_{\mu}^{\mu} R_{\nu}^{\nu} R_{\kappa}^{\kappa} R_{\lambda}^{\lambda} f_{ir} f_{js} f_{kt} f_{lu}. \end{aligned} \quad (22)$$

The important point is that here, unlike in (19), the polynomial coefficients of the strain components are *not* constants, but depend upon the equilibrium configuration ($\cdots \mathbf{R} \cdots$) imposed by the external stress. Therefore an Eulerian analog in ϵ to to equation 20, i.e. a strain polynomial with constant coefficients is not possible. The conclusion follows that the Taylor expansion of $\Phi(t)$ in the atomic displacements from equilibrium, as in (16), requires the Taylor expansion of $\phi_0(\cdots \mathbf{R} \cdots)$ in the Lagrangian strain, as in (20).

Of course, it is possible to write

$$\begin{aligned} \phi_0 = & \bar{\phi}_0 + \frac{1}{2} \bar{V} \sum \bar{c}_{ijkl} \epsilon_{ij} \epsilon_{kl} \\ & + \frac{1}{3!} \bar{V} \sum \bar{c}_{ijklmn} \epsilon_{ij} \epsilon_{kl} \epsilon_{mn} + \cdots \end{aligned} \quad (23)$$

where

$$\bar{c}_{ijkl} \equiv \frac{1}{\bar{V}} \left. \frac{\partial^2 \phi_0}{\partial \epsilon_{ij} \partial \epsilon_{kl}} \right|_0 \quad (23a)$$

and so forth. The (constants) $\bar{c}_{ijkl}$, etc. would then be related, in some complicated way, to the $\bar{\phi}_{\mu\nu}^{\mu\nu} \bar{R}_{\mu}^{\mu} \bar{R}_{\nu}^{\nu}$ and to *higher-order* terms.

This is because, according to (8b),

$$\epsilon = \eta + O(\eta^2). \quad (8c)$$

Hence the third term on the right of (23) already contains terms in η^6 . Since, as will be discussed below, it is important that the expansion (16) be truncated at the fourth-order terms, the expansion (23) is not permitted.

Consideration of this point was excluded by postulate from recent work by Thomsen and Anderson [33, 34]; these were discussions within the theoretical framework of Eulerian strain. The present conclusion is that the Lagrangian strain, rather than the Eulerian, is more fundamental to the equation of state of solids wherever thermal effects are important.

3. LATTICE DYNAMICS—THE FREE ENERGY

It is well known that, in the harmonic approximation, the Helmholtz free energy is

$$F = \phi_0 + F_s \quad (24)$$

where ϕ_0 may be taken as the first two terms of (20), and the vibrational contribution is

$$F_s = \sum_{\mathbf{k}} \left\{ \frac{\hbar \omega}{2} + kT \ln \left[1 - \exp \left(-\frac{\hbar \omega}{kT} \right) \right] \right\} \quad (25)$$

where the summation extends over all wave vectors $\mathbf{k}$ of all branches. The eigenfrequencies $\omega(\mathbf{k})$ are second derivatives of the potential energy Φ ; the spectral average is [3]

$$\overline{\omega^2} = \sum_{\mu, l} \phi_{\mu\mu}^{00} \frac{1}{M_{\mu}}. \quad (26)$$

Since, in this approximation, the $\phi_{\mu\nu}^{\text{mn}} = \bar{\phi}_{\mu\nu}^{\text{mn}}$ are constants, the ω are constant, and F_s is a function of T only. The equation of state is then

$$P = -\frac{d\phi_0}{dV}. \quad (27)$$

In the fourth-order theory, the free energy is [3]

$$F = \phi_0 + F_s + F_{anh} \quad (28)$$

where ϕ_0 is the quartic polynomial (20). F_s is of the same form (25) as in the harmonic theory, but now the frequencies are quadratic functions of the strain η . In fact, the entire term F_s must be considered to be a function of T , and a quadratic function of η [3, 6]. Incorporating the 'Grüneisen approximation' whereby strain derivatives of the logarithms of the ω are all assumed to be equal, it is [3, 6]

$$\begin{aligned} F_s(\eta, T) = & \tilde{U}_s(T) - \tilde{U}_s \sum \tilde{\gamma}_{ij} \eta_{ij} \\ & + \frac{1}{2} \sum [-\lambda_{ijkl} \tilde{U}_s + \gamma_{ij} \tilde{\gamma}_{kl} \\ & \times (\tilde{U}_s - T\tilde{C}_V)] \eta_{ij} \eta_{kl}. \end{aligned} \quad (29)$$

Other variations [13, 14] on the exact form of this approximation yield the same results in the present context. Here $\tilde{U}_s$ is the vibrational contribution to the internal energy, evaluated at the rest state; in the fourth-order approximation, it is

$$\tilde{U}_s = \sum \hbar \tilde{\omega} \left(\frac{1}{2} + \frac{1}{\exp(\hbar \tilde{\omega}/kT) - 1} \right) \quad (30)$$

$\tilde{C}_V$ is the corresponding specific heat:

$$\tilde{C}_V = \sum k \left(\frac{\hbar \tilde{\omega}}{kT} \right)^2 (e^{\hbar \tilde{\omega}/kT} - 1)^{-2} e^{\hbar \tilde{\omega}/kT} \quad (31)$$

$\tilde{\gamma}_{ij}$ is the tensor form of the Grüneisen parameter, in the rest state:

$$\tilde{\gamma}_{ij} = -\frac{1}{2} \frac{\partial \ln \tilde{\omega}^2}{\partial \eta_{ij}} \quad (32)$$

and λ is its variation with the strain:

$$\lambda_{ijkl} = -\frac{1}{2} \frac{\partial^2 \ln \tilde{\omega}^2}{\partial \eta_{ij} \partial \eta_{kl}}. \quad (33)$$

The specific anharmonic contribution F_{anh} is given in Section 10 of Leibfried and Ludwig [3]; it need not be reproduced here. As for F_s in the previous (harmonic) approximation, F_{anh} is, in the fourth-order approximation, a function of T alone. Hence it will not enter into the *thermal* equation of state (2), but only into the *caloric* equation of state, i.e. C_V and T -derivatives thereof.

The thermal equation of state which follows from (28) was first written over half a century ago [12, 13]. In its simplest form, it is called the Mie-Grüneisen (M-G) equation of state:

$$P = P_{\text{static}} + P_{\text{thermal}} \quad (34)$$

or more explicitly,

$$P = -\frac{d\phi_0}{dV} + \gamma \frac{\tilde{U}_s}{V}. \quad (35)$$

As explicitly defined by (20) and (29), it is referred to in this paper as the *fourth-order anharmonic* equation of state. It is convenient to restrict the generality of the treatment to those crystal classes whose strain response to the hydrostatic pressure is a diagonal tensor. (This includes all classes but triclinic and monoclinic.) For these cases, from (2), (28), (20), (29),

$$\begin{aligned} P = & -\frac{\tilde{V}}{3V} \sum_{\alpha=1}^3 (1 + 2\eta_{\alpha}) \left\{ \sum_{\beta} \tilde{c}_{\alpha\beta} \eta_{\beta} \right. \\ & + \frac{1}{2} \sum_{\beta\tau} \tilde{c}_{\alpha\beta\tau} \eta_{\beta} \eta_{\tau} + \frac{1}{3!} \sum_{\beta\tau\pi} \tilde{c}_{\alpha\beta\tau\pi} \eta_{\beta} \eta_{\tau} \eta_{\pi} \\ & \left. - \frac{\tilde{U}_s}{\tilde{V}} \left\{ \tilde{\gamma}_{\alpha} + \sum_{\beta} \left[\lambda_{\alpha\beta} + \tilde{\gamma}_{\alpha} \tilde{\gamma}_{\beta} \left(\frac{T\tilde{C}_V}{\tilde{U}_s} - 1 \right) \right] \right\} \right\}. \end{aligned} \quad (36)$$

Here the notation of Voigt [14] is adopted. It

is a simple matter to express the constants appearing here in terms of quantities measured in the laboratory. However, before this is done, a number of remarks of a general nature are in order.

Of basic importance is the concept of a *self-consistent approximation*. The present development specifically does *not* purport to be an exact theory, but only an approximate one. It is the requirement of internal consistency within a well-defined approximation that produces the explicit functional form (36). This equation contains *no* approximations which are not already present in the simple form (35) of the M-G equation of state. These approximations are well known; the two most important bear some discussion.

In order that the 'thermal pressure' term of (34-36) be linear in U_s , and hence linear in T at high T , it is necessary that the specific anharmonic term, F_{anh} , in (28) depend only on T , and hence vanish upon operation with $(\partial/\partial\eta)_T$. For F_{anh} to be thus constant in strain, it is necessary that ϕ_{ijkl}^{mnpq} be constant in strain, i.e. that the Coupling Parameters of *fifth-order* vanish as in (16) and (20). Thus the linearity in U_s of the thermal pressure is tied inextricably to the quartic expression in η of the static pressure. The fourth-order theory thus defined describes the thermal dependence of the lattice 'constants' and of the elastic 'constants'. It is *not* competent to describe the mixed derivative $\partial^2 K/\partial P \partial T|_0$; for that a higher-order theory is required[6].

Entirely separate from, and additional to, this approximation is the Grüneisen approximation, introducing $\bar{\omega}^2$. The simplification thereby provided is apparently crucial; little progress can be made without it. Moreover, it becomes rigorous in the high- and the low-temperature regimes[3]. However, by replacing a spectrum of functions with a single function, it thereby reduces the utility of such detailed information as *is* available. In particular, the role of the measured 'reststrahlen' frequency in this development is not clear.

4. CUBIC CRYSTALS

The fourth-order anharmonic equation of state (36) contains a number of constants, all of which are definable in terms of laboratory measurements. While this is true for all crystal classes (except, of course, monoclinic and triclinic), the cubic crystals offer the simplest and most instructive cases, and are the only ones considered in the following. For these, the strain components are equal, and from (7a)

$$\eta = \frac{1}{2} \left(\frac{a^2}{\bar{a}^2} - 1 \right) \quad (37)$$

where a is the edge of the unit cube. The incompressibility $\bar{K}$ can be written

$$\bar{K} \equiv \frac{1}{9} \sum_i^3 \bar{c}_{\alpha\beta} \quad (38)$$

analogous quantities are defined by

$$\Gamma \equiv -\frac{1}{27\bar{K}} \sum_i^3 \bar{c}_{\alpha\beta\gamma} \quad (38a)$$

$$\Lambda \equiv \frac{1}{81\bar{K}} \sum_i^3 \bar{c}_{\alpha\beta\gamma\pi} \quad (38b)$$

$$\lambda \equiv \frac{1}{9} \sum_i^3 \lambda_{\alpha\beta}. \quad (38c)$$

For this (cubic) symmetry, also[3]

$$\bar{\gamma}_{ij} = \bar{\gamma} \delta_{ij}. \quad (39)$$

The equation of state becomes

$$P = -3\bar{K} \left(\frac{a}{\bar{a}} \right)^{-1} \left\{ \eta - \frac{3}{2}\eta^2\Gamma + \frac{1}{2}\eta^3\Lambda \right\} + \frac{\bar{U}_s}{V} \left(\frac{a}{\bar{a}} \right)^{-1} \left\{ \bar{\gamma} + 3\eta \left[\lambda - \bar{\gamma}^2 \left(1 - T \frac{\bar{C}_V}{\bar{U}_s} \right) \right] \right\}. \quad (40)$$

It is easy to describe the six unknowns, $\bar{a}$, $\bar{K}$,

$\tilde{\gamma}$, Γ , λ , Λ , in terms of the six measurements, a_0 , K_0^S , α_0 , K_0' , $(\partial K/\partial T)_P|_0$, K_0'' , respectively, at the 'zero state', $P = 0$, $T = T_0 =$ room temperature[6]. In this way, an extended portion of the $P(T, V)$ surface of the solid is described by 'extrapolation' from the zero point. The value of, in fact, the necessity for such an approach (as opposed to earlier 'curve-fitting' procedures) has been emphasized by Anderson[15, 16] and others. Accordingly the constants are found by operating on (40) to yield the following iterative set:

$$0 = \eta_0 - \frac{3}{2}\Gamma\eta_0^2 + \frac{1}{2}\Lambda\eta_0^3 \quad (40a)$$

$$-\frac{U_{so}}{V\tilde{K}}\left\{\frac{\gamma}{3} + \left[\lambda - \gamma^2\left(1 - \frac{T_0 C_{v0}}{U_{so}}\right)\right]\eta_0\right\}$$

$$\tilde{K} = \frac{K_0^S \tilde{a}/a_0}{\left[1 - 3\Gamma\eta_0 + \frac{9}{2}\Lambda\eta_0^2 - \frac{U_{so}}{V\tilde{K}}(\lambda - \gamma^2)\right]} \quad (40b)$$

$$\tilde{\gamma} = \frac{\tilde{V}\alpha_0 K_0(a_0/\tilde{a})/\tilde{C}_{v0}}{[1 + 3\eta_0(\lambda/\tilde{\gamma} + \tilde{\gamma}(\partial \ln \tilde{C}_v/\partial \ln T))_0]} \quad (40c)$$

$$\lambda = \frac{\tilde{V}}{\tilde{C}_{v0} a_0} \left[\alpha_0 K_0 (K_0' - \frac{1}{3}) + \frac{\partial K^S}{\partial T} \right]_P + \gamma^2 \quad (40d)$$

$$\Gamma = \frac{K_0}{\tilde{K}} \left(\frac{\tilde{a}}{a_0} \right)^3 K_0' + 3\Lambda\eta_0 \quad (40e)$$

$$\Lambda = \frac{K_0}{\tilde{K}} \left(\frac{\tilde{a}}{a_0} \right)^3 \left[K_0 K_0'' + K_0' (K_0' + 1) - \frac{1}{9} \right] \quad (40f)$$

where α is $(\partial V/\partial T)_P/V$ and K^S is $-V(\partial P/\partial V)_S$.

This is a closed system, provided that $\tilde{U}_s$ and $\tilde{C}_v$ are known, and that all 'measurements' are actually realizable. The expressions (30) and (31) for the internal vibrational energy and the specific heat require *assumptions* on the spectrum of eigenfrequencies; Leibfried and Ludwig[3] have estimated that the use of the Debye spectrum for this purpose incurs errors smaller than those due to the errors of measurement of a_0 , K_0^S , etc. Of

course, evaluation of (30) and (31) requires the use of a characteristic temperature $\tilde{\theta}_D$ appropriate to the rest state rather than to the zero state[3, 6].

The techniques of modern laboratories are sufficient in general to measure directly all required quantities except for K_0'' . For soft materials (with small values of K_0), even this measurement may be possible[30], however it is not necessarily useful with (40). This is because for these soft materials, the interatomic forces are weak, and the displacements may become large, so that, strictly, the fourth-order anharmonic approximation is insufficient. This insufficiency is demonstrated by the fact that for these soft materials it is often also possible to measure the higher-order effects $\partial^2 K/\partial P \partial T \neq 0$, and $\lim_{T \rightarrow 0} \partial^2 K/\partial T^2 \neq 0$. The adequate description of such materials will require a higher order theory[6].

It is still possible, however, to determine the parameter Λ , and the corresponding K_0'' by indirect means. The quantities Λ and λ are both of fourth order, that is to say, they are different linear combinations of the fourth-order Coupling Parameters $\tilde{\phi}_{ijkl}^{mnop}$. In certain

cases of high symmetry, and assuming such restrictions as nearest-neighbor, central-force interaction, the quantity Λ can be calculated from λ [6]. Because of the approximations involved, however, this calculation can only be considered to provide the order of magnitude of Λ .

The parameter Λ can, however, be found exactly, if it is *assumed* that the fourth-order anharmonic approximation is sufficient to describe the solid under conditions of shock-wave compression. This assumption has, in the past, been universally adopted, with the M-G equation of state being used, along with various approximations, to interpret the Hugoniot in terms of an isotherm[32]. The assumption is not always justified, as shown below. The topic of shock-wave data will require some discussion in order to free it from a number of encumbering hypotheses;

to this end the Grüneisen parameter is treated next.

5. THE GRÜNEISEN PARAMETER

A simple differentiation of (35) yields the well-known 'thermal' formula for the Grüneisen parameter,

$$\gamma = \frac{V\alpha K}{C_V}. \quad (41)$$

Because the volume dependences of α and C_V have not been available, researchers have turned to assumptions on the nature of the vibrational spectrum in order to obtain expressions for $\gamma(V)$ [17-19]. Knopoff and Shapiro [20] have given an excellent discussion of the difficulties engendered by such assumptions. However, no such hypotheses are necessary in the present development. With the definition

$$\gamma_{ij}(V) = -\frac{1}{2}(\mathbf{1} + \mathbf{e})_{im} \frac{\partial \ln \bar{\omega}^2}{\partial \eta_{mn}} (\mathbf{1} + \mathbf{e}^\dagger)_{nj} \quad (42)$$

(of which (32) is the special case at zero strain) the Grüneisen parameter for a cubic crystal is

$$\gamma(V) = \left(\frac{V}{V_0}\right)^{2/3} (\tilde{\gamma} + 3\lambda\eta) \quad (43)$$

with the constants $\tilde{\gamma}$ and λ defined by (40c, e). Here, all the modes of vibration, both acoustic and optic, both low-frequency and high, are correctly represented by the measured values of α_0 and $(\partial K/\partial T)_P$. There are *no* assumptions in (43) beyond those already present in the simple M-G equations (35). The Grüneisen parameter is shown graphically in Fig. 2(a), using the data of Table 1, for a number of cubic materials of interest.

The calculation has also been done for non-cubic crystals, in an informal way, i.e. through the literal application of (43) and (7a) to these materials. The results are graphed in Fig. 2(b) for several materials of geologic interest. Comparison with previous work [33, 34] based on Eulerian strain emphasizes the importance of the choice of Lagrangian strain.

It is to be noted that the coefficient of $\tilde{U}_s/\tilde{V}$ in (40) contains a term additional to those of (43). It arises from the variation of U_s with compression, i.e. in this approximation,

$$U_s(V, T) = \tilde{U}_s(T) \left[1 - 3\tilde{\gamma}\eta \left(1 - \frac{T\tilde{C}_V}{\tilde{U}_s} \right) \right]. \quad (44)$$

The strain dependence of the thermal expansivity is most easily found, not from (41), but by differentiating (40) with P held constant.

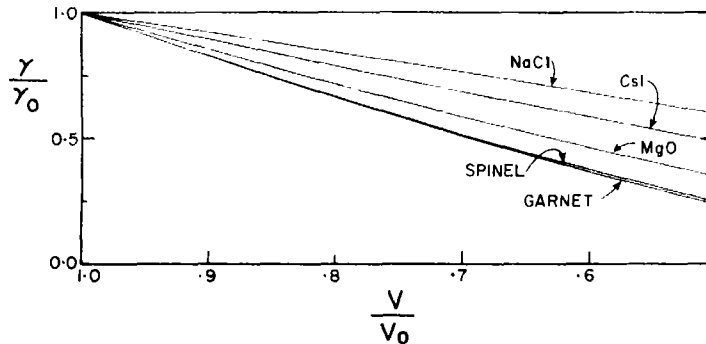


Fig. 2(a). The Grüneisen parameter, normalized to its value at $P = 0$, $T = T_0$. The basic reference value, γ_0 , is listed in Table 1.

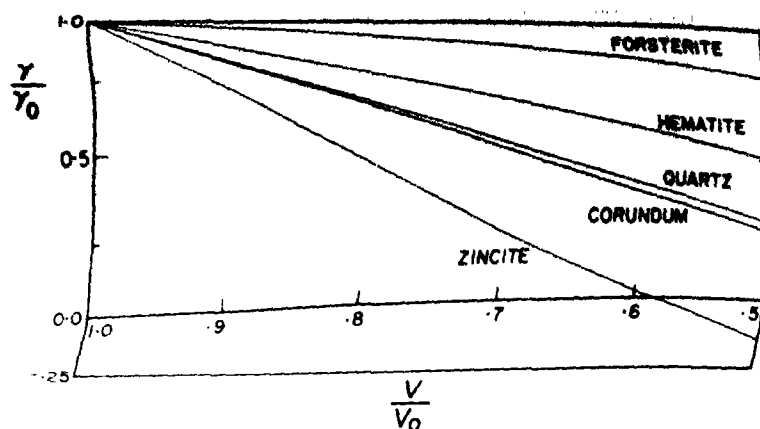


Fig. 2(b). The Gruneisen parameter, according to (5.2) normalized to γ_0 . The basic reference value γ is listed in Table 1.

Table 1. Parameters for the equation of state (40) calculated from equations 40(a-f) with the zero pressure data from the indicated source

	NaCl	MgO ^b	Spinel ^b	Garnet ^b	CsI
a (Å)	5.5705 ¹	4.1773	8.052	11.485	4.5168 ¹
K (kbar)	285.5 ¹	1733.8	2101.2	1876.6	144.8 ⁷
γ	1.566 ¹	1.752	1.08	1.13	1.535 ^b
Γ	5.09 ¹	4.51	4.2	5.28	5.36 ⁹
λ	0.559 ¹	1.355	1.29	1.10	1.061 ⁷
Λ					29.2 ⁹
n_0	327.0 ³	966.0 ⁵			118.0 ⁵
	Forsterite	Hematite ^b	Corundum ^b	Quartz ^b	Zincite ^b
a	6.600 ¹	6.672	6.312	4.808	3.617
K	1357.3 ¹⁰	2143.2	2629.7	419.0	1440.8
γ	1.05 ^b	1.93	1.35	0.49	0.65
Γ	5.25 ¹⁰	4.63	4.03	6.01	4.72
λ	0.81 ^b	2.69	1.52	0.32	1.59

¹National Bureau of Standards Circular 539, 1-9, Washington, D.C. (1953-1960)

²SLAGLE O. D. and MCKINSLEY H. A. *J. appl. Phys.* **38**, 437 (1967).

³RUBIN J., JOHNSON H. I. and ALTMAN H. W. *J. phys. Chem.* **65**, 65 (1961)

⁴BARTLE S. R. A. and SCHUEFEL D. F. *J. Phys. Chem. Solids* **26**, 537 (1965)

⁵cf. THOMSEN L., ref. [6]

⁶ANDERSON O. J., SCHRIEBER F., LIEBERMANN R. C. and SOGA N., *Rev. Geophys.* **6**, 491 (1968)

⁷SLAGLE O. D. and MCKINSLEY H. A. *J. appl. Phys.* **38**, 451 (1967).

⁸JOHNSON J. W., AGRON P. A. and BRIDG M. A. *J. Am. chem. Soc.* **77**, 2734 (1955)

⁹BARSCH G. R. and CHANG Z. P., paper presented at Symp. on the Accurate Characterization of the High Pressure Environment, Gaithersburg, Maryland (1968)

¹⁰KUMAZAWA M., unpublished data

The result is

$$\alpha(V, T) = \alpha(P=0, T) \left\{ 1 - \frac{P}{3\tilde{K}} \frac{\tilde{a}}{a} - 3\eta \left[\left(1 - \frac{1}{\tilde{\gamma}} \right) \lambda - \tilde{\gamma}^2 - \tilde{\gamma} \frac{\partial \ln C_V}{\partial \ln T} \right] \right\} \quad (45)$$

where

$$\alpha(P=0, T) = \frac{\tilde{\gamma}}{\tilde{K}\tilde{V}} \left(\frac{\tilde{a}}{a(P=0, T)} \right)^2 \tilde{C}_V(T). \quad (45a)$$

This function $\alpha(V, T)$ decreases rapidly with V ; difficulties with the fourth-order approximation may be expected near its vanishing point. In order to evaluate (45) properly, it is necessary to know P ; hence the problem of determining Λ is now discussed.

6. HUGONIOT INTERPRETATION

Through the *assumption* that the fourth-order anharmonic theory is sufficient under conditions of shock-wave compression, the parameter Λ can be evaluated. The evaluation starts with the locus of Hugoniot points in the P - V plane, where the temperature is defined implicitly by

$$U_H = U_0 + \frac{1}{2} P_H (V_0 - V_H). \quad (46)$$

The correction from Hugoniot to adiabat to isotherm is unambiguous, since $\gamma(V)$ is well defined. However, it is logically more straightforward to introduce the Hugoniot condition (46) directly into (40). The internal energy U is composed of two parts

$$U(V, T) = \phi_0(V) + U_s(V, T) \quad (47)$$

and in the fourth-order theory, U_s is defined by (44) and (30). ϕ_0 is, from (20),

$$\phi_0(V) = \tilde{K}\tilde{V} \left[\frac{(-3)^2}{2!} \eta^2 + \frac{(-3)^3}{3!} 1 \eta^3 + \frac{(-3)^4}{4!} \Lambda \eta^4 \right]. \quad (48)$$

Substitution of (46) *et seq* into (40) gives the fourth-order Hugoniot:

$$P_H = - \frac{\partial \phi_0}{\partial V_H} \bigg|_H + \gamma(V_H) \left[\frac{1}{2} P_H \left(\frac{V_0}{V_H} - 1 \right) - \frac{\phi_0(V_H)}{V_H} + \frac{U_0}{V_H} \right]. \quad (49)$$

When evaluated at a single Hugoniot point, (P_H, V_H) , this equation contains only one unknown, Λ , which is thereby determined. The equation can then be used to generate the entire locus of Hugoniot points. Further, the same constants can be used in (40) to generate the isotherms, adiabats, etc.

This method of Hugoniot interpretation is equivalent in concept to more complicated schemes [21-23]; it has, however, the advantage of internal consistency. It shares with these other methods the assumption of the fourth-order approximation; as discussed below, this assumption is not always justified. Only partial checks on the assumption are possible within the conceptual framework developed so far. The Hugoniot generated from (49) does, in fact, reproduce the measured Hugoniot within experimental error (for all minerals tested), but this is perhaps to be expected, because of the fitting procedure used. Another measure of the validity of this assumption is introduced in the next section.

7. EQUATIONS OF STATE OF NaCl and MgO

The calculation of the equations of state of NaCl and MgO was made for reasons of mutual comparison. Weaver *et al.* [26] statically compressed a powdered mixture of NaCl and MgO and simultaneously measured the lattice constant of each. Hence equation (40), when applied to this simultaneous compression data, should give the same calculated pressure for both solids.

The constants for NaCl in Table 1 were used in conjunction with the shock-wave data of Fritz *et al.* [24] to determine $\Lambda_{\text{NaCl}} = 23$. The constants for MgO were used with the

shock-wave data of Carter *et al.* to determine $\Lambda_{\text{MgO}} = 22 \pm 4$. The postulation of a simple strength effect (cf. [22]) in MgO was not required to fit the Hugoniot data. The uncertainty in Λ_{MgO} , which results from scatter in the Hugoniot points, is not important for calculations below $P = 300$ kb. The (analytically) calculated isotherms are given in Table 2 and compared with those given by Weaver *et al.*; the agreement is good. The advantages of the present theory over that of Weaver *et al.*, and of Decker [25, 28], include: (1) its internal consistency, (2) its easy extension to the description of arbitrarily complex crystals, and (3) its lack of limiting hypotheses (for example, no central-force theory can describe the elasticity of NaCl completely, as is known from measurements on the individual elastic moduli. On the other hand, the present theory is easily extendable to the description of the elastic moduli; such a paper is now in preparation.)

It is an interesting exercise to calculate that part, P_Λ , of the pressure which is due to the quartic term in the strain, with coefficient Λ . It is plotted, as a fraction of P , in Fig. 3. Because of the larger compression of NaCl at a given pressure, P_Λ is considerably greater for this mineral than for MgO. In fact, by 300 kbar, P_Λ for NaCl is too great to be realistically considered a perturbation term. A serious doubt may be entertained as to the sufficiency of the present fourth-order theory

Table 2. Simultaneous compression of NaCl and MgO at 298°K. P [26] is from Weaver *et al.* [26], in kb

NaCl			MgO		
V/V_0	P	P [26]	V/V_0	P	P [26]
0.911	28	28 ± 1	0.983	29	28 ± 5
0.764	124	122 ± 2	0.940	114	115 ± 6
0.735	154	154 ± 3	0.928	141	142 ± 7
0.700	198	199 ± 3	0.907	194	196 ± 7
0.692	208	211 ± 3	0.902	207	211 ± 8
0.679	228	232 ± 4	0.895	227	232 ± 8
0.671	240	246 ± 4	0.888	248	251 ± 8
0.662	254	262 ± 4	0.884	259	265 ± 9

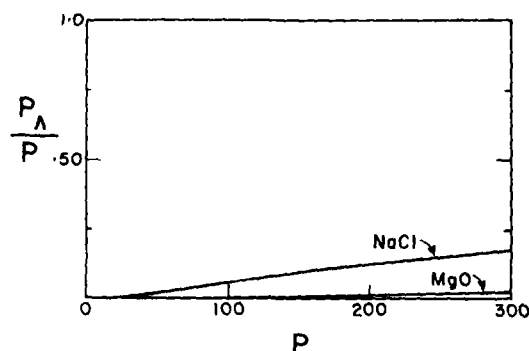


Fig. 3. The contribution of the fourth-order term, P_Λ , to the equation of state (40) for NaCl and MgO.

in this case. The fact that the present calculations do not indicate such an insufficiency is not at present well understood.

The sign of the second derivative K''_0 has been the subject of some speculation [11, 16, 12] and at least one measurement [30], the consensus being that it is generally small and negative. With the parameter Λ determined by the Hugoniot for NaCl and MgO, K''_0 is given directly by (40f). It is, for NaCl, $\bar{K}K''_0 = -3.79$; for MgO, $\bar{K}K''_0 = -3 \pm 4$. Thus the present work is in accord with the current consensus.

8. DISCUSSION

The fourth-order anharmonic (thermal) equation of state is given by (36) and (40). Especially for cubic minerals, there is no particular difficulty. Of the six parameters which characterize the equation, five are routinely measured at zero pressure; the sixth is easily obtained from the Hugoniot. The Grüneisen parameter is unambiguously defined by (43).

The sufficiency, however, of the fourth-order theory is another matter entirely. As Chang and Barsch [30] have remarked, the series (20) converges slowly. It seems reasonable to expect that the fourth-order approximation will begin to break down before $V/V_0 \approx 0.8$. This is in accord with an estimate

[31] that melting (and hence breakdown of the approximation) occurs when the vibrational amplitude approaches $a_0/10$. These compressions will occur near $P/K_0 \sim \frac{1}{3}$. Thus, for a soft material with weak interatomic forces, and hence a small incompressibility, the range of validity of the fourth-order theory should be restricted. For a harder material, the range will be correspondingly extended; for most oxides and silicates the theory is expected to be adequate below their points of transition to higher density phases. It can, of course, also be applied to the high pressure phases, if the relevant data are available. Eventually, one may hope to be able to understand in this way the equation of state of the homogeneous lower mantle of the earth.

For these harder materials, however, the Grüneisen approximation may lead to trouble. This is because, by virtue of their hardness, θ_D is greater than room temperature, and the normal modes of vibration are not all saturated. The approximation may be drastic, and may be reflected in false values of the constants, leading perhaps to effects such as the slight divergence of the isotherms in Table 2 at intermediate compressions. It may be preferable, for these materials, to evaluate $\bar{K}$, etc. with measurements at high temperature rather than at T_0 . In this case, however, the intrinsic errors of measurement will be higher, and it may be that no advantage accrues. The situation should be separately evaluated in every case.

Acknowledgements—The author is thoroughly indebted to O. I. Anderson for his continued guidance and encouragement. I also benefited greatly from many discussions with R. C. Liebermann, and from a critical correspondence with T. Takahashi. In a more specific sense, I am grateful to Leon Knopoff and to G. F. Duval for forcefully pointing out to me, at a time when I was not prepared to believe it, the ambiguity in the theory of finite strain. Financial support was provided through National Aeronautics and Space Administration contract NSG-445 and through Air Force Office of Scientific Research contract F44620-68-C-0079.

REFERENCES

1. TRUESDELL C. and NOLL W., *Handb. Phys.*, Vol. III/3, Springer, Berlin (1965).
2. TRUESDELL C., *The Mechanical Foundations of Elasticity and Fluid Dynamics*, Gordon and Breach, New York (1966).
3. LEIBFRIED G. and LUDWIG W., *Solid State Physics*, Vol. 12, p. 275, Academic Press, New York (1961).
4. MURNAGHAN F. D., *Finite Deformation of an Elastic Solid*, Wiley, New York (1951).
5. MURNAGHAN F. D., *Am. J. Math.* **59**, 235 (1937).
6. THOMSEN L., Ph.D. Thesis, Columbia University, New York (1969).
7. KNOPOFF L., *J. geophys. Res.* **68**, 2929 (1963).
8. BIRCH F., *J. appl. Phys.* **9**, 279 (1938).
9. BIRCH F., *Bull. seis. Soc. Am.* **29**, 463 (1939).
10. BIRCH F., *Phys. Rev.* **71**, 809 (1947).
11. BIRCH F., *J. geophys. Res.* **57**, 227 (1952).
12. GRUNEISEN E., *Ann. Phys.* **39**, 257 (1912).
13. GRUNEISEN E., *Handb. Phys.*, Vol. 10, p. 1, Springer, Berlin (1926). Also, in translation, NASA Reproduction RE-2-18-59W.
14. BORN M. and HUANG K., *Dynamical Theory of Crystal Lattices*, Oxford University Press, London (1954).
15. ANDERSON O. L., *J. Phys. Chem. Solids* **27**, 547 (1966).
16. ANDERSON O. L., *Phys. Earth Planet. Inter.* **1**, 169 (1968).
17. SLATER J. C., *Introduction to Chemical Physics*, McGraw-Hill, New York (1939).
18. DUGDALE J. S. and MACDONALD D. K. C., *Phys. Rev.* **89**, 832 (1953).
19. ALT'SCHULER I. V., *Soviet Phys. Usp.* **8**, 52 (1965).
20. KNOPOFF L. and SHAPIRO J. N., *J. geophys. Res.* **74**, 1439 (1969).
21. TAKEUCHI H. and KANAMORI H., *J. geophys. Res.* **71**, 3985 (1966).
22. AHRENS T. J., ANDERSON D. L. and RINGWOOD A. E., *Rev. Geoph.* **7**(4), 667 (1969).
23. SHAPIRO J. N. and KNOPOFF L., *J. geophys. Res.* **74**, 1435 (1969).
24. FRITZ J. N., MARSH S. P., CARTER W. J., and MCQUEEN R. G., paper presented at *Symp. on the Accurate Characterization of the High Pressure Environment*, Gaithersburg, Maryland (1968).
25. DECKER D. L., unpublished.
26. WEAVER J. S., TAKAHASHI T. and BASSETT W. A., paper presented at *Symp. on the Accurate Characterization of the High Pressure Environment*, Gaithersburg, Maryland (1968).
27. CARTER W. J., MARSH S. P., FRITZ J. N. and MCQUEEN R. G., paper presented at *Symp. on the Accurate Characterization of the High Pressure Environment*, Gaithersburg, Maryland (1969).
28. DECKER D. L., *J. appl. Phys.* **36**, 157 (1965).
29. SCHWARTZSCHILD M., *Structure and Evolution of the Stars*, Princeton University Press, Princeton (1958).

30. CHANG Z. P. and BARSCH G. R., *Phys. Rev. Lett.* **19**, 1381 (1967).
31. GILVARRY J. J., *Phys. Rev.* **102**, 308 (1955).
32. RICE M. H., MCQUEEN R. G. and WALSH J. M., *Solid State Physics*, Vol. 6, p. 1. Academic Press, New York (1958).
33. THOMSEN L. and ANDERSON O. L., *J. geophys. Res.* **74**, 981 (1969).
34. THOMSEN L. and ANDERSON O. L., paper presented at *Symp. on the Accurate Characterization of the High Pressure Environment*, Gaithersburg, Maryland (1968).

QUANTUM MECHANICAL TREATMENT OF POLAR OPTICAL MODE MOBILITY AND APPLICATION TO InSb*†

R. W. CUNNINGHAM and J. B. GRUBER

Department of Physics, Washington State University, Pullman, Wash. 99163, U.S.A.

(Received 15 September 1969; in revised form 17 December 1969)

Abstract—A manifestly quantum mechanical calculation of the electrical conductivity for polar optical mode lattice scattering of carriers has been carried out by application of a Kubo formula. Fröhlich's interaction Hamiltonian has been used in an S matrix approximation scheme. The resulting conductivity is then found to lie above the corresponding classical expression when the temperature is below the characteristic temperature, as expected. However, for temperatures above the characteristic temperature the conductivity lies below the classical expression and is contrary to expectation. When both calculations are compared to mobility data for heavy holes in InSb, the quantum calculation gives a better fit to the data. Experimentally it is found that the dominant lattice scattering for heavy holes is the polar mechanism for $T < 300^\circ\text{K}$, above 300°K a second mechanism contributes to the scattering and is tentatively identified as non-polar optical mode scattering. The identification is complicated by the fact that the carrier optical mode coupling constant and the optical mode characteristic temperature are both unknown.

1. INTRODUCTION

THE PROBLEM of electrical conduction in solids has been considered by many workers in the past. Lucid treatments based on the semiclassical Boltzmann transport equation may be found in the works of Wilson[1], Ziman[2], and Beer[3]. A manifestly quantum mechanical approach has been suggested by Kubo[4]. His theory does not depend on a transport equation or a distribution function, but does employ the density operator of quantum theory. The Kubo theory has been increasingly employed in the study of solids. This paper is an attempt to apply a manifestly quantum mechanical theory of conductivity to the problem of polar optical mode mobility in solids.

Previously Howarth and Sondheimer[5] have developed the theory of polar optical mode mobility by use of a variational solution of the Boltzmann equation. The form of their

solution yields a value for the conductivity and mobility which approach true values asymptotically from below. The dependence of solution on the form of the trial functions has not been investigated in general and is another impetus for a quantum mechanical investigation.

This paper will be concerned with a calculation of the mobility of carriers scattered by polar optical mode lattice vibrations through the use of a Kubo formula. First an approximation scheme based on the work of Fujita and Abe[6] will be obtained so that the current calculation which appears in the Kubo formula may be evaluated. The evaluation scheme is field theoretic and comes from an expansion of the scattering matrix. Next the Fröhlich[7] interaction Hamiltonian will be transformed to number operator form and used in the evaluation scheme. A specific expression will then be obtained for the electrical conductivity and mobility. Comparison of the quantum and semiclassical solutions will be made. Finally the quantum mechanical results will be applied to the

*Part of a thesis submitted in partial fulfillment of the Ph.D. degree by R. W. Cunningham.

†Supported by United States Atomic Energy Commission Contract Number USAEC AT(45-1)-2012.

heavy hole mobility in InSb. The quantum calculation is in better agreement with experimental values than the semiclassical theory over a fairly wide temperature range.

2. THE KUBO FORMULA AND AN EVALUATION SCHEME

The form of the Kubo[4] formula for the electrical conductivity most appropriate for this work is

$$\sigma_{ij}(0) = \beta V \int_0^\infty d\tau \langle J_i(\tau) J_j \rangle, \quad (1)$$

where $\sigma_{ij}(0)$ is the ij th component of the zero frequency ($\omega = 0$) conductivity tensor, $\beta^{-1} = k_B T$ with k_B Boltzmann's constant and T the absolute temperature, V the volume of the specimen, τ a time parameter, and $\langle J_i(\tau) J_j \rangle$ is defined by

$$\langle J_i(\tau) J_j \rangle = Tr \{ \rho_0 J_i(\tau) J_j \} \quad (2)$$

Here the J 's are one particle current operators and ρ_0 is the equilibrium density operator for the grand canonical ensemble and is defined by

$$\rho_0 = z^{-1} e^{-\beta(H + \mu N)} \quad (3)$$

and

$$z = Tr e^{-\beta(H + \mu N)}, \quad (4)$$

H is the steady state Hamiltonian of the system and includes the carrier-lattice vibration interaction, μ is the electrochemical potential and N is the carrier density. The grand canonical ensemble is the most appropriate one to use since the phonon and particle densities are constantly fluctuating. A detailed derivation of equation (1) has been given by Cunningham[8]

With the aid of the evolution operator $J_i(\tau)$ may be written

$$J_i(\tau) = e^{iH\tau/\hbar} J_i(0) e^{-iH\tau/\hbar}. \quad (5)$$

But the evolution operator may be written in

terms of the scattering matrix[9] as

$$e^{-iH\tau/\hbar} = e^{-iH_{cl}\tau/\hbar} S(\tau), \quad (6)$$

where

$$H_{cl} = H_{\text{carrier}} + H_{\text{lattice}}, \quad (7)$$

$S(\tau)$ is the scattering matrix given by

$$S(\tau) = \sum_{n=0}^{\infty} (-1)^n \int_0^\tau dt_1 \cdots \int_0^{t_{n-1}} dt_n \{ H_I(t_1) \cdots H_I(t_n) \}, \quad (8)$$

and H_I is the interaction Hamiltonian evaluated at the time indicated by its argument. The form of the various terms in H_{cl} and H_I will be considered in due course. Then the current correlation may be written

$$\langle J_i(\tau) J_j \rangle = \langle S^\dagger(\tau) e^{iH_{cl}\tau/\hbar} J_j e^{-iH_{cl}\tau/\hbar} S(\tau) J_i \rangle. \quad (9)$$

The argument of J_j has been suppressed since it is no longer pertinent.

The most appropriate form for J_i and J_j is as number operators. A representative current density is

$$J_x = \left[\frac{e\hbar}{m^*V} \right] \sum_k k a_k^\dagger a_k, \quad (10)$$

where $a_k^\dagger$ and a_k are carrier creation and destruction operators, and e is the magnitude of the electronic charge. This form is obtained by assuming bands of standard form, an assumption which will be used throughout. However, the effective mass m^* is a weighted effective mass and is not necessarily the cyclotron mass. The current correlation may then be written as

$$\langle J_i(\tau) J_j \rangle = \left[\frac{e\hbar}{m^*V} \right]^2 \sum_{\vec{k}, \vec{k}'} C(\tau, \vec{k}, \vec{k}') \quad (11)$$

where $C(\tau, \vec{k}, \vec{k}')$ is defined by

$$C(\tau, \vec{k}, \vec{k}') = \langle S^\dagger(\tau) a_{\vec{k}'}^\dagger(\tau) a_{\vec{k}}(\tau) S(\tau) a_{\vec{k}}^\dagger a_{\vec{k}'} \rangle \quad (12)$$

and

$$\tilde{O}(\tau) \equiv e^{iH_0\tau/\hbar} O e^{-iH_0\tau/\hbar} \quad (13)$$

is an interaction representation for any operator O . When equation (12) is expanded by use of equations (2) and (3) and rearranged with the aid of a theorem of quantum field theory [10], $C(\tau, \vec{k}, \vec{k}')$ becomes

$$C(\tau, \vec{k}, \vec{k}') = \langle a_{\vec{k}'} S^\dagger(\tau) \tilde{a}_{\vec{k}}(\tau) \tilde{a}_{\vec{k}}(\tau) S(\tau) a_{\vec{k}'}^\dagger \rangle \times e^{-i\mu(E_{\vec{k}} - \mu)\tau} \quad (14)$$

Evaluation of equation (14) follows from Wick's theorem [11] which may be written for this case as

$$\langle ABC \cdots YZ \rangle = (\pm 1)^{\delta_1} \langle AB \rangle \langle C \cdots YZ \rangle + (\pm 1)^{\delta_2} \langle AC \rangle \langle BD \cdots YZ \rangle + \cdots \quad (15)$$

where δ_r ($r = 1, 2, 3$) is the parity of the permutation required to obtain the given arrangement, $(+1)$ for Bosons and (-1) for Fermions. Each of the multicomponent averages may be reduced to a two component average (or contraction). Application to equation (14) yields

$$C(\tau) = \{ \langle a_{\vec{k}'} S^\dagger(\tau) \rangle \langle \tilde{a}_{\vec{k}} \tilde{a}_{\vec{k}} S(\tau) a_{\vec{k}'}^\dagger \rangle + \cdots + \langle a_{\vec{k}'} a_{\vec{k}'}^\dagger \rangle \langle S^\dagger(\tau) \tilde{a}_{\vec{k}} \tilde{a}_{\vec{k}} S(\tau) \rangle \} e^{-i\mu(E_{\vec{k}} - \mu)\tau} \quad (16)$$

The rules for evaluation of the two component contractions have been given by Fujita and Abe [6] as

$$\begin{aligned} \langle a_{\vec{k}'}(u) a_{\vec{k}'}^\dagger(u') \rangle &= \delta(\vec{k}, \vec{k}') (1 - f_{\vec{k}}) e^{-i\mu(u - u')/\hbar} \\ \langle a_{\vec{k}'}^\dagger(u') a_{\vec{k}}(u) \rangle &= \delta(\vec{k}, \vec{k}') f_{\vec{k}} e^{-i\mu(u - u')/\hbar} \\ \langle b_{\vec{q}}(u) b_{\vec{q}'}^\dagger(u') \rangle &= \delta(\vec{q}, \vec{q}') (1 + n_{\vec{q}}) e^{-i\omega_{\vec{q}}(u - u')} \\ \langle b_{\vec{q}'}(u') b_{\vec{q}}(u) \rangle &= \delta(\vec{q}, \vec{q}') n_{\vec{q}} e^{-i\omega_{\vec{q}}(u - u')} \end{aligned} \quad (17)$$

where $f_{\vec{k}}$ and $n_{\vec{q}}$ are the Fermi-Dirac and Bose-Einstein functions respectively,

$$f_{\vec{k}} = [e^{\mu(E_{\vec{k}} - \mu)/\hbar} + 1]^{-1}$$

$$n_{\vec{q}} = [e^{\beta\hbar\omega_{\vec{q}}} + 1]^{-1}. \quad (18)$$

In addition, there is the rule that all contractions containing an odd number of factors vanish. The rules given by equations (17) imply a propagation direction with u' a creation and u a destruction vertex. If the opposite is true, even though $u > u'$, a minus must be attached to the $E_{\vec{k}}$ or $\omega_{\vec{q}}$. For the cases to be considered in this work, only $\omega_{\vec{q}}$ will be affected.

3. THE INTERACTION HAMILTONIAN

Evaluation of the contractions requires a form for the interaction Hamiltonian. This has been carried out by Fröhlich [7] who obtained

$$H_I = \kappa \sum_{\vec{q}} \frac{1}{q} \left[b_{\vec{q}} e^{-i\vec{q} \cdot \vec{r}} - b_{\vec{q}}^\dagger e^{i\vec{q} \cdot \vec{r}} \right], \quad (19)$$

where $\vec{q}$ is a phonon wave vector of magnitude q , $\vec{r}$ is a position vector (r is the 'distance' between a phonon and a carrier), $b_{\vec{q}}$ and $b_{\vec{q}}^\dagger$ are phonon creation and destruction operators respectively, and

$$\kappa = \left[\frac{4\pi e^*}{V_u} \left(\frac{\hbar}{2M\omega_l G} \right)^{1/2} \right]. \quad (20)$$

Here e^* is the Callen [12] effective charge, V_u the volume of a unit cell, M the reduced mass of the two lattice ions, ω_l the optical mode angular frequency, and G the number of unit cells in the specimen. When equation (19) is rewritten in terms of carrier number operators it becomes

$$H_I = \kappa \sum_{\vec{k}, \vec{q}} \frac{1}{q} (a_{\vec{k}}^\dagger a_{\vec{k}+\vec{q}} b_{\vec{q}}^\dagger - a_{\vec{k}+\vec{q}}^\dagger a_{\vec{k}} b_{\vec{q}}). \quad (21)$$

Note that H_I contains an odd number of operators in each term, a fact that will be used later. Fujita and Abe [6] have considered a diagrammatic representation for this type of Hamiltonian.

Note that conservation laws are written into the subscripts of equation (21). The first term

indicates the creation of a phonon of momentum $\bar{q}$, the destruction of a carrier of momentum $\bar{k} + \bar{q}$, and the creation of a carrier of momentum $\bar{k}$.

The derivation of equation (21) has assumed single phonon carrier interactions. Multi-phonon process may be included, but at this stage of theoretical development their inclusion does not seem appropriate. Only single phonon-carrier interactions will be considered in this paper.

4. APPROXIMATE EVALUATION OF THE CURRENT CORRELATION

For computational convenience, equation (14) may be rewritten as

$$C(\tau, k, k') = u(\tau) e^{i\mathbf{R} \cdot (\mathbf{k} - \mathbf{k}')} \quad (22)$$

where $u(\tau)$ is given by

$$u(\tau) = \langle a_k S^\dagger(\tau) \tilde{a}_k(\tau) \tilde{a}_l(\tau) S(\tau) a_{k'} \rangle, \quad (23)$$

and the arguments $\bar{k}$ and k' have been suppressed in u . When $u(\tau)$ is expanded to a sum of products of two component contractions and evaluated by equation (17), the result is

$$u(\tau) = \delta(\bar{k}, \bar{k}') (1 - f_k) (1 - f_{k'}) \langle S^\dagger S \rangle + \delta(\bar{k}', \bar{k}) (1 - f_{k'}) f_k \langle S^\dagger S \rangle. \quad (24)$$

The argument τ has been suppressed.

The remaining contraction is most easily carried out when S and $S^\dagger$ are expanded according to equation (8), so that

$$\langle S^\dagger S \rangle = \sum_{r,n=0}^{\infty} \langle S_r^\dagger S_n \rangle = \sum_{\substack{(r,n) \\ r \text{ integer}}}^{\infty} \langle S_r^\dagger S_n \rangle, \quad (25)$$

where S_r or $S_r^\dagger$ is just the r th term of the expansion indicated by equation (8). When equation (25) is written out in detail it becomes

$$\langle S_r^\dagger S_n \rangle = (i)^{r+n} \int_0^\tau dt_1 \cdots \int_0^{\tau-t_{r-1}} dt_r \int_0^\tau dt_1 \cdots \int_0^{\tau-t_{n-1}} dt_n \langle H_1 \cdots H_1 H_1 \cdots H_n \rangle \quad (26)$$

where

$$H_r = H_I(t_r).$$

Expansion of the interaction Hamiltonian to a sum of complete two-element contractions yields

$$\begin{aligned} \langle H_1 \cdots H_1 H_1 \cdots H_n \rangle &= \langle H_j H_{j-1} \rangle \\ &\times \langle H_{j-2} \cdots H_n \rangle + \cdots + \langle H_j H_n \rangle \\ &\times \langle H_{j-1} \cdots H_{n-1} \rangle \\ &= \langle H_j H_{j-1} \rangle \cdots \langle H_{n-1} H_n \rangle \\ &+ \langle H_j H_n \rangle \cdots \langle H_{n-2} H_{n-1} \rangle. \end{aligned}$$

In general $\langle H_j H_n \rangle$ may be evaluated by the use of equation (21). The notation will be simplified for convenience by suppressing

$$\kappa \sum_{kq} \frac{1}{q}$$

in the next several steps, and setting $\bar{k} = K$, $\bar{k} + \bar{q} = K'$, and the subscript q will be dropped from the phonon creation and destruction operators. Then

$$\begin{aligned} \langle H_j H_n \rangle &= \langle (a_{K'}^\dagger a_{K'} b_j^\dagger - a_{K'}^\dagger a_{Kj} b_j) (a_{Kn}^\dagger a_{Kn} b_n^\dagger \\ &\quad - a_{K'n}^\dagger a_{Kn} b_n) \rangle \\ &= \langle a_{K'n}^\dagger a_{K'} b_j^\dagger a_{Kn}^\dagger a_{K'} b_n^\dagger + a_{K'n}^\dagger a_{Kj} b_j a_{K'n}^\dagger a_{Kn} b_n \\ &\quad - a_{K'n}^\dagger a_{Kj} b_j a_{Kn}^\dagger a_{K'n} b_n^\dagger - a_{K'n}^\dagger a_{Kn} b_j^\dagger a_{K'}^\dagger a_{Kn} b_n \rangle \\ &= -\langle a_{K'n}^\dagger a_{K'n} \rangle \langle a_{Kj} a_{Kn} \rangle \langle b_j b_n^\dagger \rangle \\ &\quad - \langle a_{Kj}^\dagger a_{Kn} \rangle \langle a_{K'n}^\dagger a_{K'n} \rangle \langle b_j^\dagger b_n \rangle \\ &= -f_{K'} (1 - f_K) e^{-i(t_n - t_j)(E_{K'} - E_K + \hbar\omega_q)/\hbar} (n_q + 1) \\ &\quad - f_K (1 - f_{K'}) n_q e^{-i(t_n - t_j)(E_K - E_{K'} + \hbar\omega_q)/\hbar}. \quad (27) \end{aligned}$$

The $\pm$ occurs with $\hbar\omega_q$ because either t_n or t_j may be the creation vertex for the phonon. Let $F_1 = f_{K'} (1 - f_K) (n_q + 1)$, $F_2 = f_K (1 - f_{K'}) n_q$, and

$$\epsilon_\pm = (E_K - E_{K'} \pm \hbar\omega_q)/\hbar \quad (28)$$

so that $\langle H_j H_n \rangle$ may be written

$$\langle H_1 H_n \rangle = -F_1 e^{i(t_1 - t_1)\epsilon_+} - F_2 e^{-i(t_1 - t_1)\epsilon_-}. \quad (29) \quad \langle H_4 H_3 H_2 H_1 \rangle = \langle H_4 H_3 \rangle \langle H_2 H_1 \rangle$$

Integrations over the t_r may be carried out with the aid of the asymptotic formula[6]

$$\int_0^\alpha dt_i \int_0^{t_i} dt_j \frac{t_j^{P-1}}{(P-1)!} e^{\pm i(t_i - t_j)} = \frac{\pi \alpha^P}{P!} \delta_\pm(\epsilon) + O(\alpha^{P-1}), \quad (30)$$

where

$$\delta_\pm(\epsilon) = \delta(\epsilon) \pm \frac{i}{\pi} PP(1/\epsilon); \quad (31)$$

δ is the Dirac delta function, and PP means the principal part is to be taken. Application of equation (30) to a general term such as equation (29) is complicated, but systematic application through a few terms will illustrate the general result.

Consider first $\langle S_2^\dagger \rangle$ and $\langle S_2 \rangle$. From equation (8)

$$\begin{aligned} \langle S_2^\dagger(\tau) \rangle &= -\int_0^\tau dt_1 \int_0^{t_1} dt_2 H_2 H_1 \\ \langle S_2(\tau) \rangle &= -\int_0^\tau dt_1 \int_0^{t_1} dt_2 \langle H_1 H_2 \rangle \end{aligned}$$

and from equation (29)

$$\begin{aligned} \langle H_2 H_1 \rangle &= -[F_1 e^{i(t_1 - t_2)\epsilon_+} + F_2 e^{-i(t_1 - t_2)\epsilon_-}] \\ \langle H_1 H_2 \rangle &= -[F_1 e^{-i(t_1 - t_2)\epsilon_+} + F_2 e^{i(t_1 - t_2)\epsilon_-}], \end{aligned}$$

application of equation (30) yields

$$\begin{aligned} \langle S_2^\dagger(\tau) \rangle &= \int_0^\tau dt_1 \int_0^{t_1} dt_2 [F_1 e^{i(t_1 - t_2)\epsilon_+} \\ &\quad + F_2 e^{-i(t_1 - t_2)\epsilon_-}] \\ &\sim \pi\tau [F_1 \delta_+(\epsilon_+) + F_2 \delta_-(\epsilon_-)] \quad (32a) \end{aligned}$$

$$\begin{aligned} \langle S_2(\tau) \rangle &= \int_0^\tau dt_1 \int_0^{t_1} dt_2 [F_1 e^{-i(t_1 - t_2)\epsilon_+} \\ &\quad + F_2 e^{i(t_1 - t_2)\epsilon_-}] \\ &\sim \pi\tau [F_1 \delta_-(\epsilon_+) + F_2 \delta_+(\epsilon_-)]. \quad (32b) \end{aligned}$$

Further consider $\langle S_4^\dagger(\tau) \rangle$ which involves $\langle H_4 H_3 H_2 H_1 \rangle$.

$$+ \langle H_4 H_2 \rangle \langle H_3 H_1 \rangle + \langle H_4 H_1 \rangle \langle H_3 H_2 \rangle.$$

Since the contractions are ordinary numbers they may be manipulated at will. The first term is then straight-forward and yields the integral

$$\begin{aligned} \int_0^\tau dt_1 \int_0^{t_1} dt_2 \langle H_2 H_1 \rangle \int_0^{t_2} dt_3 \int_0^{t_3} dt_4 \langle H_4 H_3 \rangle \\ = \frac{(\pi\tau)^2}{2!} [F_1 \delta_+(\epsilon_\pm) + F_2 \delta_-(\epsilon_\pm)]^2, \end{aligned}$$

the second set of integrals having yielded a πt_2 factor. The term $\langle H_4 H_2 \rangle \langle H_3 H_1 \rangle$ is most easily evaluated by straight-forward evaluation. The final result is

$$\langle S_4^\dagger(\tau) \rangle \sim \frac{(\pi\tau)^2}{2!} [F_1 \delta_+(\epsilon_\pm) + F_2 \delta_-(\epsilon_\pm)]^2, \quad (33)$$

so that the general trend should be apparent.

$\langle S^\dagger S \rangle$ may then be approximated as

$$\langle S^\dagger S \rangle \approx \sum_{n=0}^{\infty} (S_n^\dagger + S_n) \sim e^{-\Gamma(K, K')} \quad (34)$$

where

$$\Gamma(K, K') = \pi [F_1 \delta(\epsilon_\pm) + F_2 \delta(\epsilon'_\pm)] \quad (35)$$

and

$$\delta(X) = \delta_+(X) + \delta_-(X). \quad (36)$$

Equation (35) is written in such a form because an ϵ_+ may occur in one term and ϵ_- in the other, as will be seen later.

Equation (35) may be further evaluated when the suppressed notation is written out in full, with the result

$$\Gamma(k) = \frac{\pi \kappa^2 V}{(2\pi)^3} \int \frac{1}{q^2} [F_1 \delta(\epsilon_\pm) + F_2 \delta(\epsilon'_\pm)] d^3 q, \quad (37)$$

where the transformation

$$\sum_q \rightarrow [V/(2\pi)^3] \int d^3 q$$

has been used. Transformation to polar coordinates simplifies equation (37) to

$$\Gamma(k) = \frac{\pi\kappa^2 V}{(2\pi)^3} \int dq \int d\Omega [F_1 \delta(\epsilon_+) + F_2 \delta(\epsilon_-)],$$

and as usual, $d\Omega = \sin \theta d\theta d\phi$. In general, $\bar{k}$ and $\bar{q}$ do not lie in the same direction, and it is convenient to let θ be the angle between k and $\bar{q}$ ($\bar{k} \cdot \bar{q} = \cos \theta$) so that

$$\Gamma(k) = \frac{\pi\kappa^2 V}{(2\pi)^2} \int dq \int \sin \theta [F_1 \delta(\epsilon_+) + F_2 \delta(\epsilon_-)] d\theta.$$

The limits of integration for θ are obtained from the requirement that $\cos \theta$ be real. From equation (28), and the definition of K' and K, ϵ_+ may be written

$$\epsilon_+ = \left[\frac{\hbar^2}{2m^*} (q^2 + 2kq \cos \theta) \pm \hbar\omega_q \right] / \hbar \quad (38)$$

where the bands of standard form assumption,

$$E_k = \hbar^2 k^2 / 2m^*,$$

and

$$E_{k'} = \hbar^2 (k'^2 + q^2 + 2kq \cos \theta) / 2m^*$$

have been used. Since the integral will have a contribution only when ϵ_+ and ϵ_- are zero due to the δ functions, the limits are found from

$$1 \pm \frac{(\hbar\omega_q)(2m^*/\hbar^2) - q^2}{2kq} = 1. \quad (39)$$

It will be shown later that the signs of ϵ_+ and ϵ_- are opposite and will therefore yield two different limits for the integrals. For the present the solutions of equation (39) will be designated q_1, q_2, q'_1, q'_2 for the two limits. Upon change of variables to $y = [\hbar(q^2 + 2kq \cos \theta) / 2m^*] \pm \hbar\omega_q$, $\Gamma(k)$ may be written

$$\Gamma(k) = - \left[\frac{2m^*}{\hbar} \right] \frac{\pi\kappa^2 V}{(2\pi)^2} \int_{q_1}^{q_2} F_1 \frac{dq}{2kq} \int \delta(y) dy$$

$$+ \int_{q'_1}^{q'_2} F_2 \frac{dq}{2kq} \int \delta(y) dy$$

$$= - \frac{m^* \pi \kappa^2 V}{\hbar (2\pi)^2} [F_1 \ln(q_2/q_1) + F_2 \ln(q'_2/q'_1)]. \quad (40)$$

Equation (23) now becomes

$$u(\tau) = [\delta(k', k)(1 - f_k)^2 + \delta(k', k')\delta(k, k) \times (1 - f_{k'})f_k] e^{-\tau/\tau(k)}. \quad (41)$$

In general both terms will be present in the evaluation of equation (41). However, if f_k is assumed large, $f_k \sim 0$, then only the second term is large. This assumption will be used throughout the rest of this work, and equation (41) becomes

$$u(\tau) = \delta(k', k')\delta(k, k)f_k e^{-\tau/\tau(k)}. \quad (42)$$

5. APPROXIMATION FOR THE CONDUCTIVITY TENSOR

The conductivity tensor for the carrier-polar optical phonon interaction may be approximated with the aid of the foregoing. In order to draw all of the ideas together, an outline of the calculation will be shown. Equation (1) gives the zero frequency conductivity tensor as

$$\sigma_{ij} = \beta V \int_0^\infty d\tau \langle J_j(\tau) J_i \rangle. \quad (1)$$

But the current correlation function is found to be

$$\langle J_j(\tau) J_i \rangle = \left(\frac{e\hbar}{m^* V} \right)^2 \sum_{k, k'} k_i k'_j C(\tau) \delta(\bar{k}, \bar{k}'),$$

and $C(\tau)$ is given by equation (22) as

$$C(\tau) = u(\tau) e^{-\beta(E_{k'} - \mu)} \quad (22)$$

and $u(\tau)$ has the value

$$u(\tau) = \delta(k, k)\delta(k', k') e^{-\tau/\tau(k)f_k}. \quad (42)$$

The combination of these equations yields

$$\sigma_{ij} = \beta V \left(\frac{e\hbar}{m^*V} \right)^2 \times \sum_{k,k'} \int_0^\infty \delta(k,k') k_\alpha k'_\beta e^{-\beta(E_{k'} - \mu)} e^{-\tau \Gamma(k')} f_k d\tau. \quad (43)$$

Equation (43) is easily integrated over τ to obtain

$$\sigma_{ij} = \beta V \left(\frac{e\hbar}{m^*V} \right)^2 \times \sum_{k,k'} f_k \delta(k',k) k_\alpha k'_\beta e^{-\beta(E_k - \mu)} / \Gamma(k').$$

One summation will delete the δ function and the conductivity tensor becomes

$$\sigma_{ij} = \frac{\beta V^2}{(2\pi)^3} \left(\frac{e\hbar}{m^*V} \right) \int d^3k f_k \frac{k_\alpha k_\beta}{\Gamma(k)} e^{-\beta(E_k - \mu)}. \quad (44)$$

For cubic and isotropic materials $k^2 = k_1^2 + k_2^2 + k_3^2$, $k_1^2 = k_2^2 = k_3^2$, so that $k_\alpha k_\beta = k^2/3$. Then transformation to spherical polar coordinates and energy variables yields

$$\sigma = \frac{\beta}{3(2\pi)^3} \left(\frac{e\hbar}{m^*} \right)^2 \left(\frac{m^*}{\hbar^2} \right) \left(\frac{2m^*}{\hbar^2} \right)^{3/2} \times 4\pi \int_0^\infty \frac{f_E E^{3/2} e^{-\beta(E - \mu)}}{\Gamma(E)} dE.$$

Further simplification is possible with the introduction of the dimensionless parameter x defined by $x = \beta E$ so that the conductivity

where

$$F(z) = \int_0^\infty \frac{f_x x^2 e^{-x} dx}{F_1 \ln \left(\frac{q_2}{q_1} \right) + F_2 \ln \left(\frac{q'_2}{q'_1} \right)} \quad (46)$$

and $z = \theta/T = \hbar\omega_l/kT$ which is contained in F_1 and F_2 . Single band conduction has been assumed throughout the above development. However, if the band in which conduction takes place is spin degenerate, equation (45) should be multiplied by two. It is also worth noting that equation (45) is equivalent to equation (43) of Ref. [5], but that $G(z)$ has been replaced by $F(z)$.

Evaluation of $F(z)$ is straightforward. For terms involving F_1 the process is such that $+ \hbar\omega_l$ is chosen, but for F_2 terms $- \hbar\omega_l$ is chosen. Then q_1, q'_1, q_2, q'_2 may be evaluated and the ratios indicated in equation (40) become

$$\frac{q_2}{q_1} = \frac{\sqrt{1 + \hbar\omega_l/E} + 1}{\sqrt{1 + \hbar\omega_l/E} - 1} = \frac{\sqrt{1 + z/x} + 1}{\sqrt{1 + z/x} - 1},$$

$$\frac{q'_2}{q'_1} = \frac{1 + \sqrt{1 - \hbar\omega_l/E}}{1 - \sqrt{1 - \hbar\omega_l/E}} = \frac{1 + \sqrt{1 - z/x}}{1 - \sqrt{1 - z/x}}. \quad (47)$$

Here $z = \hbar\omega_l/k_B T = \theta/T$ and θ is a characteristic temperature. In keeping with the approximations introduced for f_k and $f_{k'}$, F_1 and F_2 are

$$F_1 = e^{\beta(E - \mu + \hbar\omega_l)} (n+1), \quad F_2 = e^{-\beta(E - \mu)} n.$$

Since $n+1 = n e^{\beta\hbar\omega_l}$ and $f_x = e^{-\beta(E - \mu)}$, $F(z)$ becomes

$$F(z) = \frac{1}{n} \int_0^\infty \frac{x^2 e^{-x} dx}{\ln \left\{ \frac{\sqrt{1 + z/x} + 1}{\sqrt{1 + z/x} - 1} \right\} + h \left(\frac{z}{x} - 1 \right) \ln \left\{ \frac{1 + \sqrt{1 - z/x}}{1 - \sqrt{1 - z/x}} \right\}} \quad (48)$$

eventually becomes

$$\sigma = \frac{2M v_l V_a e^{\beta\mu}}{3\pi^2 \hbar^2 e^{*2} \beta^2} F(z), \quad (45)$$

where $h(z/x - 1)$ is the Heavyside step function defined by $h(y) = 0$ if $y \leq 0$ and $h(y) = 1$ if $y > 0$. The properties of the $\ln$ functions may be used to rewrite equation (48) in a

more tractable form as

$$F(z) = \frac{1}{2n} \int_0^{\infty} \frac{x^2 e^{-x} dx}{\ln \{y + \sqrt{(y^2 + 1)}\} + h(y-1) \ln \{y + \sqrt{y^2 - 1}\}}, \quad (49)$$

where $y = \sqrt{x/z}$. Then the conductivity becomes

$$\sigma = \frac{2M\nu_l V_a (e^z - 1) e^{\beta\mu}}{3\pi^2 h^2 e^{*2} h^2} G(z) \quad (50)$$

with $G(z)$ defined by

$$G(z) \equiv \int_0^{\infty} \frac{x^2 e^{-x} dx}{\ln \{y + \sqrt{(y^2 + 1)}\} + h(y-1) \ln \{y + \sqrt{y^2 - 1}\}}. \quad (51)$$

Spin degeneracy of the band has been included in equation (50) since it obtains for most semiconductors.

$G(z)$ has been evaluated numerically and a plot is shown in Fig. 1. For comparison the related quantity of Howarth and Sondheimer [5] is included. It should be noted that $G(z)$ lies above the calculation of Ref. [5] for $Z > 0.5$ as expected. However, for $0 \leq Z \leq 0.5$, the calculation of Ref. [5] lies above the calculation performed here. This is somewhat unexpected and is probably due to the type of statistics employed. Similar results are obtained in Ref. [5] for a degenerate carrier distribution, but a direct comparison of the two computations is difficult.

The mobility of charge carriers may be obtained from the relationship

$$\sigma = Ne\mu \quad (52)$$

where N is the density of carriers and μ is their mobility. For carriers in a band of standard form and the relationship

$$N = \frac{2}{(2\pi)^3} \int f_0 d^3k,$$

where f_0 is given by equation (18), the classical approximation to N is

$$N = \frac{2}{h^3} (2\pi m^* k_B T)^{3/2} e^{\beta\mu}. \quad (53)$$

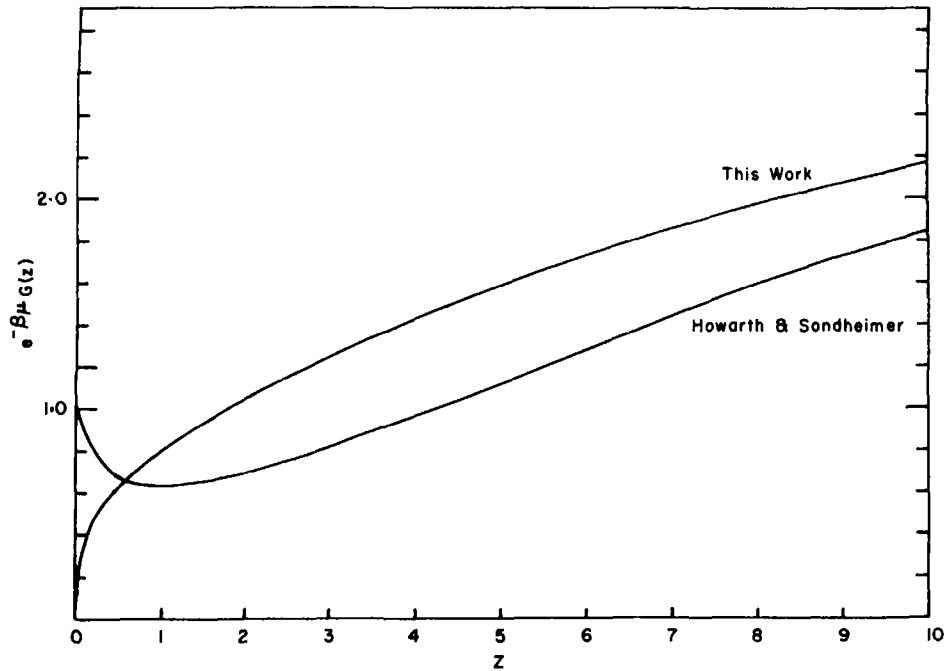
Thus the mobility becomes

$$\mu = \sigma/Ne = \frac{2^{3/2} \hbar M \nu_l V_a (k_B T)^{1/2} (e^z - 1)}{3\pi^{1/2} m^{*3/2} e e^{*2}} G(z). \quad (54)$$

6. APPLICATION TO THE MOBILITY OF HOLES IN InSb

Carriers in III-V compounds may be scattered in a variety of ways. In addition to scattering by lattice vibrations, impurity scattering may be effective. In this section it will be assumed that the samples which will be studied are sufficiently pure so that scattering by lattice vibrations dominate. Then four types of lattice scattering need to be considered. (1) polar optical mode, (2) deformation potential, (3) non-polar optical mode, and (4) piezoelectric. The first mechanism has been discussed above. The second mechanism is due to the interaction of carriers with the acoustic modes of lattice vibration. Non-polar optical mode scattering will arise when the type III or V atoms only vibrate in an optical mode. Piezoelectric scattering arises when long wavelength polarized acoustic modes interact with a carrier.

The polar optical mode mobility is given by equation (54), and values of the parameters for InSb are $M = 9.81 \times 10^{-23}$ g, $\nu_l = 197.2$ cm⁻¹, $e^* = 0.16$, and $V_a = 68.0 \times 10^{-24}$ cm³


 Fig. 1. The function $G(z)$ as a function of z .

[15]. Then the polar optical mode mobility takes on the value

$$\mu = 11.1 T^{1/2} (e^{(284/T)} - 1) G(284/T) / (m^*/m_0)^{3/2} \quad (\text{cm}^2/\text{v-sec}), \quad (55)$$

The deformation potential mobility is given by [16]

$$\mu_d = 3.2 \times 10^{-5} C_{11} (m_0/m^*)^{5/2} / E_d^2 T^{3/2} \quad (\text{cm}^2/\text{v-sec}),$$

where C_{11} is the elastic constant in the $\langle 110 \rangle$ direction in units of dyn/cm², m_0 is the free electron mass, m^* the conductivity mass, and E_d the deformation potential in eV. C_{11} has the value 6.717×10^{11} dyn/cm² [17] and E_d is estimated from $E_{ac} - E_d = E$ with $E = -7.2$ eV and $|E_{ac}| = 8.25$ eV [18] as $E_d = -1.1$ eV. Then μ_d becomes

$$\mu_d = 2.04 \times 10^7 (m_0/m^*)^{5/2} T^{-3/2}. \quad (56)$$

Harrison's [19] theory of piezoelectric scattering yields

$$\mu_\pi = 1.05 C_{11} K^2 e_{14}^2 (m_0/m^*)^{3/2} T^{-1/2} \quad (\text{cm}^2/\text{v-sec}),$$

where e_{14} is the piezoelectric constant (in esu/cm²). For InSb $K = 16.8$ [20] and $e_{14} = 2.13 \times 10^4$ esu/cm² [21] so that μ_π becomes

$$\mu_\pi = 4.4 \times 10^5 (m_0/m^*)^{3/2} T^{-1/2} \quad (\text{cm}^2/\text{v-sec}), \quad (57)$$

Ehrenreich and Overhauser [22] have considered the theory of non-polar optical mode mobility. Their work

$$\mu_{np} = 1.35 \times 10^{17} \rho a^2 \theta^3 (m_0/m^*)^{5/2} F(\eta) / C_4^2 T^{5/2} \quad (\text{cm}^2/\text{v-sec}),$$

where ρ is the mass density, a the lattice constant (in cm), C_1 the coupling constant between non-polar optical modes and carriers (in eV), and $F(w)$ the function defined by

$$F(w) = \int_0^w \frac{w' e^{-\theta w'}}{\phi(w'^{-1})} dw' \quad (58)$$

where

$$\phi(w^{-1}) = n(1+w^{-1})^{1/2} + (n+1)(1-w^{-1})^{1/2}, \quad \text{for } w > 1$$

$$n(1+w^{-1})^{1/2}, \quad \text{for } w < 1$$

and $n = (e^{\theta a^2} - 1)^{-1}$. For InSb the mobility becomes

$$\mu_{np} = 3.26 \times 10^3 \theta^3 (m_0/m^*)^{-1/2} F(w) / C_1^2 T^{3/2} \quad (\text{cm}^2/\text{v-sec}). \quad (59)$$

The experimental mobility for holes in InSb is shown in Fig. 2. Some of the data was obtained explicitly for this work, but data from other sources[23-26] is included for comparison. Examination of the figures shows that over a fairly wide temperature range the mobility of all the samples is the same. The close agreement of the experimental data for samples from so many sources thus indicates lattice scattering is dominant for $T = 150^\circ\text{K}$, at least for pure samples.

In order to estimate the applicability of each of the four mechanisms, the low temperature value $m^* = 0.43m_0$ has been used[8]. Piezoelectric scattering may be ruled out immediately since $\mu_\pi(300^\circ\text{K}) = 9.3 \times 10^5 \text{ cm}^2/\text{v-sec}$, or more than a thousand times the measured mobility and rises more steeply than the experimental points. Deformation potential scattering also runs above the experimental values by a factor of at least 10 and also does not have the same temperature dependence as the experimental values. Therefore it cannot be the most dominant mechanism. The non-polar mobility contains the unknown quantity C_1 , if θ has the same value as the polar optical mode θ . Equation (59) then yields a reason-

able fit to the experimental mobility only if C_1 has an abnormally large value as compared to other materials. Finally, equation (55) has been fitted to the experimental mobility by allowing m^* to be an adjustable parameter. The fit obtained is shown by heavy dots in Fig. 2 for $m^* = 0.45m_0$. Reasonably good agreement is obtained. In contrast, the semiclassical fit of Ref. [5] falls considerably higher at the higher temperatures.

A constant effective mass has been assumed in the discussion above. However, Cunningham[8] has found the heavy hole mass to be temperature dependent. When his values for (m^*/m_0) are used in equation (55), an improved fit having no adjustable parameters is obtained. Comparison between the experimental points and computed values is shown in Fig. 2. The agreement is quite good over about 150°K temperature range, the poor agreement at low temperatures being due to a small amount of impurity scattering[23]. The analysis has only been carried out to 300°K since that temperature represents the high temperature limit of the data used to obtain (m^*/m_0) .

An attempt has been made to fit the higher temperature experimental points with a combination of polar and non-polar mobilities through the simple expedient of adding reciprocal mobilities. Additional experimental points due to Schoenwald[24] extending to 750°K have been included to aid in the fit. Reasonable results are obtained for $m^* = 0.45m_0$ only when θ is allowed to increase to 350°K . Then C_1 takes on the value 12 eV which is in reasonable agreement with other materials. The fit of the two optical mode mechanisms to the experimental points is shown in Figs. 2 and 3. An improved fit may be obtained if both θ and C_1 are increased.

The combination of polar and non-polar optical mode mobilities must be regarded as highly speculative since very little is known about either C_1 or θ . They are at best a pair of adjustable parameters as far as this work is concerned. In addition, the theory of non-

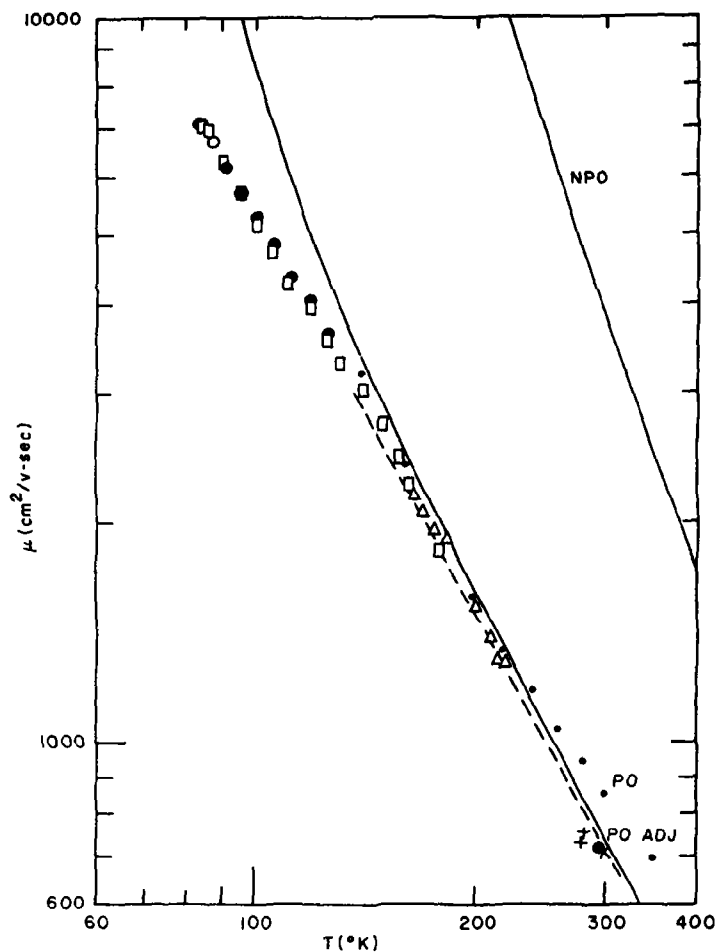


Fig. 2. Experimental and theoretical mobilities as a function of temperature. The polar mobility for a temperature independent conductivity mass is indicated by dots, data from Refs. [23], [24], [25] and [26] have been included.

polar mobility has been adapted from the theory for elemental semiconductors and may not be completely applicable to III-V compounds. For such compounds the non-polar optical modes arise from second nearest neighbors and then for two lattices having the same lattice constant but different masses. Thus the value of the non-polar coupling constant may be quite different from the value for the column IV semiconductors, and the characteristic temperature may not be the

same as for the polar modes. The most meaningful statement is that for temperatures below 300°K polar optical mode scattering is dominant; above 300°K an additional mechanism or mechanisms may be operative but is as yet not well understood.

7. CONCLUSION

A quantum mechanical theory of conductivity and mobility for polar optical mode lattice scattering has been developed. For

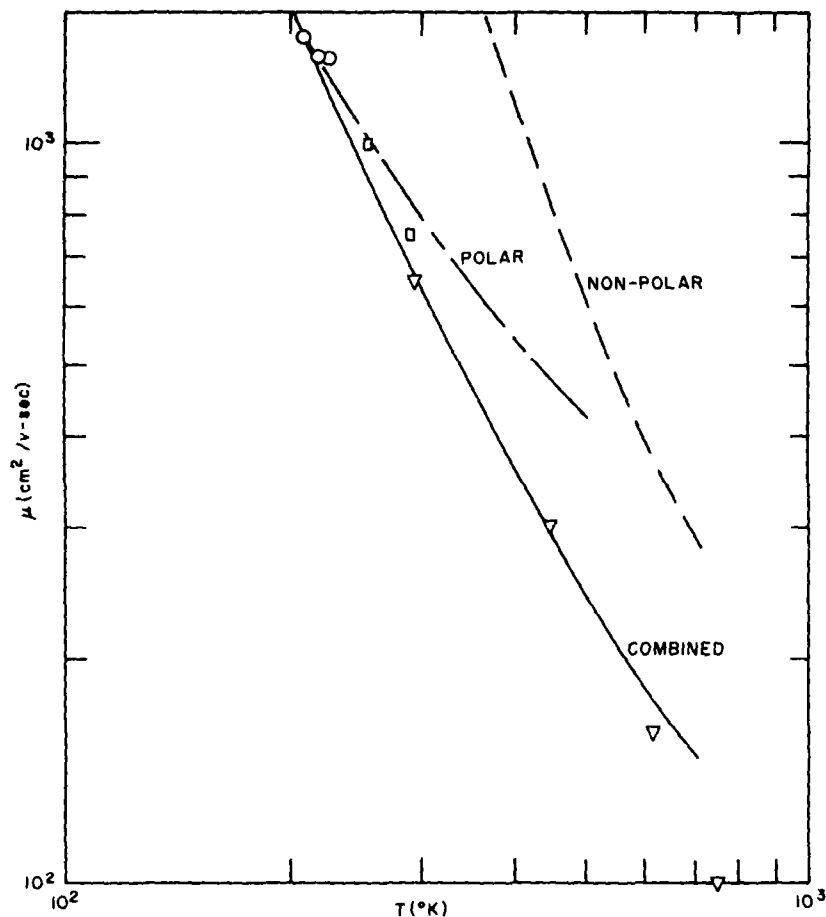


Fig. 3. Polar and non-polar optical mode mobilities extended to high temperatures.

temperatures below the polar optical mode characteristic temperature the two theories are in agreement, but for $T > \theta$ the quantum mechanical calculation has an essentially different behavior. This divergence of the quantum and semiclassical theories is somewhat unexpected. The source of the difference has not been investigated, but is believed to stem from the quantum nature of the problem. When the two are compared to experimental results for holes in InSb, the quantum mechanical calculation fits the data better than the semiclassical theory.

The theory has also been used to investigate

the dominant lattice scattering mechanism for holes in InSb. For $150^\circ\text{K} \leq T \leq 300^\circ\text{K}$ polar optical mode scattering is dominant, and for $T > 300^\circ\text{K}$ a combination of polar and non-polar optical mode scattering seems to fit the experimental data fairly well. Identification of the non-polar mode is, however, quite speculative since both the coupling constant and characteristic temperature must be used as adjustable parameters to effect a reasonable fit.

Acknowledgements—The authors are indebted to Professor James L. Park for many helpful conversations. He also served as testor for some of the theoretical ideas.

REFERENCES

- 1 WILSON A. H., *The Theory of Metals* Cambridge University Press, London (1953).
- 2 ZIMAN J., *Electrons and Phonons*, Oxford University Press, London (1960).
- 3 BEER A. C., *Galvanomagnetic Effects in Semiconductors*, Chap. 1 Academic Press, New York (1963).
- 4 KUBO R., *J. phys. Soc. Japan* **12**, 570 (1957).
- 5 HOWARTH D. J. and SONDHEIMER E. H., *Proc. R. Soc. A* **219**, 53 (1953).
- 6 FUJITA S. and ABE R., *J. Math. Phys.* **3**, 350 (1962).
- 7 FROHLICH H., *Adv. Phys.* **3**, 325 (1954).
- 8 CUNNINGHAM R. W., Thesis, Washington State University (1969), unpublished.
- 9 MANDL F., *Introduction to Quantum Field Theory*, Chaps. 5 and 12 Interscience, New York (1959).
- 10 MATTUCK R. D., *A Guide to Feynman Diagrams in the Many-Body Problem*, pp. 113–259, McGraw-Hill, New York (1967). I am indebted to Professor Fujita for bringing this to my attention.
- 11 MANDL F. (Ref. [9]), pp. 1–22; MATTUCK R. D. (Ref. [10]), p. 262.
- 12 CALLEN H. B., *Phys. Rev.* **76**, 1394 (1949).
- 13 DWIGHT H. B., *Tables of Integrals and Other Mathematical Data*, equations (602.2) and (602.4), Macmillan, New York (1947).
- 14 HASS M. and HENVIS B. W., *J. Phys. Chem. Solids* **23**, 1099 (1962).
- 15 STRAUMANIS M. E. and KIM C. D., *J. appl. Phys.* **36**, 3822 (1965).
- 16 BARDEEN J. and SHOCKLEY W., *Phys. Rev.* **77**, 407, (1950).
- 17 The compressibility has been computed from the elastic constants via the relationship for cubic materials: $K = 3/(C_{11} + 2C_{12})$. The values obtained are derived from the constants given by Madelung; MADELUNG O., *Physics of III-V Compounds*, p. 345, Wiley, New York (1964).
- 18 PURI S. M., *Phys. Rev.* **139**, A995 (1965).
- 19 HARRISON W. A., *Phys. Rev.* **101**, 903 (1956).
- 20 MADELUNG O. (Ref. [17]), p. 101.
- 21 ARLT G. and QUADFLIEG P., *Phys. Status Solidi* **25**, 323 (1968).
- 22 EHRENREICH H. and OVERHAUSER A. W., *Phys. Rev.* **104**, 331 and 649 (1956).
- 23 CUNNINGHAM R. W., HARPE E. and BULLIS W. M., *Proc. Int. Conf. of the Phys. of Semiconductors*, p. 732 The Institute of Physics and the Physical Society, London (1962).
- 24 SCHOENWALD H., *Z. Naturf.* **19a**, 1276 (1964).
- 25 HOWARTH D. J., JONES R. H. and PUTLEY E. H., *Proc. phys. Soc.* **70B**, 124 (1957).
- 26 HIERONYMUS H. and WEISS H., *Solid-St. Electron* **5**, 71 (1962).

Note added in proof

We wish to thank the referee for calling our attention to a paper by Yu. B. Ermolovich (*Soviet Phys.-solid St.* **11**, 429 (1969)) which appeared after submission of our paper. Ermolovich indicated the deformation mobility due to both longitudinal and transverse modes follows $\mu_d = 7.55 \times 10^6 T^{-3/2}$. However, we find the longitudinal contribution to be $\mu_{dl} = 1.5 \times 10^6 T^{-3/2}$ and the transverse contribution to be $\mu_{dt} = 2.0 \times 10^7 T^{-3/2}$ which yield $\mu_d = 1.8 \times 10^7 T^{-3/2}$. μ_{dt} was computed from the constants $C_{44} = 3.018 \times 10^{11}$ dyn/cm² [17] and $E_{dt} = 2.0$ eV (F. H. Pollak, private communication). Ermolovich has estimated $E_{dt} = 2.3$ eV which lowers μ_d to $1.5 \times 10^7 T^{-3/2}$. He also estimated E_{dl} as $E_{dl} = -9.4$ eV, a value which lowers our estimate for μ_{dl} below the low temperature experimental points. The main differences between the two calculations of μ_d are the values of the effective mass and the longitudinal deformation potential. Further elucidation of this will best be carried out after an unambiguous determination of E_d .

INTERBAND MAGNETOREFLECTION OF α -Sn*

S. H. GROVES†

Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, Mass. 02173, U.S.A.

C. R. PIDGEON

Francis Bitter National Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, Mass. 02139, U.S.A.

A. W. EWALD and R. J. WAGNER‡§

Northwestern University, Evanston, Ill. 60201, U.S.A.

(Received 24 November 1969)

Abstract—Two sets of oscillations in the magnetoreflexion of high purity α -Sn have been observed. These are well explained by the 'inverted' band structure. The $\Gamma_8^+ - \Gamma_7^-$ energy separation is found to be 0.413 eV, and independent of temperature over the range 1.5°–85°K. Other directly determined quantities are the band-edge masses $m_e^*(\Gamma_8^+) = 0.028m$, $m_e^*(\Gamma_8^+) = 0.195m$, and $m_e^*(\Gamma_7^-) = 0.058m$; the $\mathbf{k} \cdot \mathbf{p}$ interaction parameter F_p and the valence-band spin-orbit splitting Δ are deduced to be 24.0 and 0.80 eV, respectively. The results of this and other experiments raise doubts about 'current thoughts' on the positions of the Γ_{15} conduction band and Γ_{15} valence band. There is a discrepancy between interband and intraband effective masses, which is also characteristic of InSb.

1. INTRODUCTION

(a) α -Sn Review

α -Sn is the heaviest member of the group 4, diamond structure semiconductors. Because the α phase of Sn is stable only below 13°C, crystal growth and handling problems have impeded studies of this material in comparison to those of Ge and Si. Transformation of β -Sn crystals by cooling usually produces only α -Sn powder because of the large increase in volume in the $\beta \rightarrow \alpha$ transition. It has been possible to produce small volume pieces such as filaments and foils, and the early experiments were done on these as well

as on powder. These experiments have been reviewed by Busch and Kern[1]. In 1958 Ewald and Tufte[2] produced small but high quality single crystals of α -Sn by solution growth in Hg at $\approx -30^\circ\text{C}$. The purity of these crystals was as good as that of the β -Sn source material, giving $5\text{--}10 \times 10^{15}$ donors/cm³; although heavier n -type and p -type dopings could be obtained if desired. Later developments, to be described below, made it possible to increase the purity of the α -Sn by more than an order of magnitude over the β -Sn source material, reducing the donor concentration to $\approx 5 \times 10^{14}$ cm⁻³.

The availability of single crystal α -Sn has led to many definitive experiments. Several of direct relevance to our experiment are mentioned here and in later sections, and the reader is referred to a recent review[3] for a fuller account. Figure 1 shows a portion of the band structure of α -Sn for the highest valence bands and lowest conduction band. This 'inverted' band structure was suggested by Groves and Paul[4] to explain the follow-

This work was sponsored by the Department of the Air Force at Lincoln Laboratory, supported by the U.S. Air Force Office of Scientific Research at the Francis Bitter National Magnet Laboratory, and jointly supported by the Advanced Research Projects Agency and the National Science Foundation at Northwestern University.

*Visiting Scientists, Francis Bitter National Magnet Laboratory, M.I.T., Cambridge, Mass. 02139, U.S.A.

†Present address, Naval Research Laboratory, Wash. D.C. 20380 U.S.A.

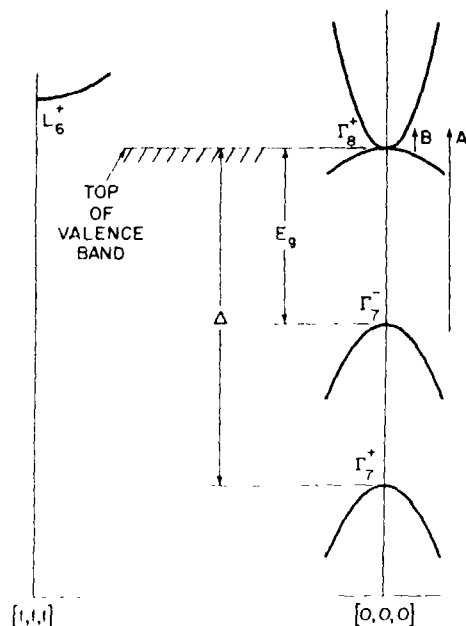


Fig. 1. Partial band structure of α -Sn showing the highest valence bands and lowest conduction band (which includes L_6^+ and Γ_8^+). Arrows A and B indicate the two sets of interband transitions discussed here.

ing distinctive experimental observations: (1) A magnetoresistance measured by Tufte and Ewald[5], which for n -type samples has $\langle 000 \rangle$ symmetry at low temperatures (due to electrons in the Γ_8^+ conduction band) and $\langle 111 \rangle$ symmetry at high temperatures (due to electrons in the L_6^+ minima), and for p -type samples has $\langle 000 \rangle$ symmetry; (2) A $T^{3/2}$ dependence for the intrinsic activation of carriers at low temperatures (appropriate to activation across a zero energy gap) which does not change with pressure because hydrostatic pressure does not split the Γ_8^+ degeneracy[4]; (3) A high temperature intrinsic activation appropriate to an energy gap of 0.1 eV[1], caused by thermal ionization dominated by the Γ_8^+ valence band and the L_6^+ conduction band. (The $L_6^+ - \Gamma_8^+$ energy separation at low temperatures has been determined recently by Lavine and Ewald [6, 3] to be 0.092 eV.) (4) A conduction band

effective mass, measured by Hinkley and Ewald, appropriate to a 'mass energy gap' of several tenths of an eV, rather than appropriate to an energy gap of ≈ 0 eV[7]. That is, the mass is determined largely by the magnitude of the $\Gamma_7^- - \Gamma_8^+$ spacing, and while this is the same as the thermal energy gap in a material such as InSb, it is not in the band structure of Fig. 1. Recent experiments bearing directly on the Γ_8^+ valence and conduction band degeneracy are the determination of the warping of the Γ_8^+ conduction band, by Booth and Ewald[8, 3], and the effects of uniaxial stress, by Roman and Ewald[9, 3].

(b) Magnetoreflexion

In the magnetoreflexion experiment reported here two sets of oscillations in the reflection as a function of magnetic field are attributed to transitions between Landau levels in the Γ_7^- and Γ_8^+ bands and in the Γ_8^+ valence and conduction bands, as shown by arrows A and B, respectively, in Fig. 1[10]. These results are similar to those on HgTe [11, 12], another material with the 'inverted' band structure.

The theory of the magnetic energy levels derives from the effective mass theory of Luttinger and Kohn[13, 14] and a generalization of this to the 'small-gap' problem by Pidgeon and Brown[15]. Reference[14] gives the solution of the coupled Γ_8^+ effective-mass Hamiltonian (applied to cyclotron resonance in p -type Ge). This includes the 'quantum effects' or irregular spacings of the Landau levels near the Γ_8^+ degeneracy energy. The treatment in Ref.[15] includes the Γ_7^+ and Γ_7^- bands as well, and thus accounts for the nonparabolicity in $E(\mathbf{k})$ from the $\Gamma_7^- - \Gamma_7^+ - \Gamma_8^+$ $\mathbf{k} \cdot \mathbf{p}$ interactions and the 'quantum effects'. The magnetic Hamiltonian of Ref. [15] is equally applicable to the inverted structure, $E(\Gamma_8^+) > E(\Gamma_7^-)$, and the more usual case, $E(\Gamma_7^-) > E(\Gamma_8^+)$, as is the corresponding zero field Hamiltonian[16]. We have found a greater departure from linear behavior of photon energy vs. magnetic field, $h\nu$ vs. H ,

for the $\Gamma_8^+ \rightarrow \Gamma_8^+$ transitions than is introduced by the $\Gamma_7^- - \Gamma_8^+ - \Gamma_8^+ \mathbf{k} \cdot \mathbf{p}$ interactions. In an attempt to explain this we have extended the treatments of Refs.[14] and [15] to include the Γ_8^- and Γ_6^- conduction bands (from the Γ_{15} single group, conduction band).

The magnetoreflexion data permit a direct evaluation of the $\Gamma_8^+ - \Gamma_7^-$ energy separation. In addition, by adjusting the parameters in the effective mass Hamiltonian to fit the predicted transition energies to those observed, one obtains effective masses for both Γ_8^+ bands and the Γ_7^- band. Although the Γ_7^+ band is not involved in the transitions, it is coupled into the Hamiltonian and an estimate of mass for that band is found as well as the $\Gamma_8^+ - \Gamma_7^+$ energy separation.

2. EXPERIMENTAL DETAILS AND RESULTS

(a) Sample preparation

Single crystals of α -Sn grown from Hg solution by the method described in Ref.[2] have smooth, natural facets which are well suited for reflectivity studies. For our measurements we used the highest purity α -Sn which is produced by further purification of the best commercially available β -Sn (Cominco six-nine) by a solvent extraction technique: The $\beta \rightarrow \alpha$ transition at -35°C of a wt.% Hg alloy with Sn yields massive chunks of α -Sn. This material, placed in contact with liquid Hg, absorbs additional Hg (approximately 25 per cent by volume) as the temperature is raised to 4°C . The Hg, saturated with Sn, is extracted by lowering the temperature to -15°C . Finally, the purified tin is reclaimed from solution by cooling to -35°C . This procedure reduces the n type impurity content (determined by Hall measurements) from $\sim 8 \times 10^{15} \text{ cm}^{-3}$ to $\sim 5 \times 10^{11} \text{ cm}^{-3}$. As will be seen below, the quality of the magneto-optical data from this material is comparable to that from the best Ge and InSb.

(b) Measurement details

The data presented below were obtained from a sample with a (100) plane facet,

measuring about $6 \text{ mm} \times 3 \text{ mm}$. All measurements were taken in the Faraday configuration, with the optical propagation vector along the magnetic field. The data are thus characteristic of the magnetic field perpendicular to the (100) plane.

The magnetoreflexion was measured with the sample in several dewar configurations. The 1.5°K runs were made with the sample submerged in superfluid helium, optical access being achieved with a cold sapphire window cut perpendicular to the c -axis. The same arrangement was used at 77°K , with the sample submerged in liquid nitrogen. Because of the absorption of the sapphire window the submerged sample technique was restricted to wavelengths shorter than 6μ . For the measurements at longer wavelengths the sample was mounted on the cold finger of a liquid helium dewar equipped with a KBr window. The sample temperature in this configuration was about 20°K . It was found that with the cold finger at -10 to -15°C the sample could be held safely in the α -phase and the dewar evacuated in a reasonable length of time. The temperature was monitored with a thermocouple and the dewar tail was cooled with CO_2 'snow' produced by throttling liquid CO_2 .

A plane polarizer (AgCl_2 pile of plates or wire grid) and a CsI Fresnel rhomb were used to obtain circularly polarized radiation. Switching from one Faraday component of radiation to the other was accomplished by reversing the direction of $\mathbf{H}$. The reflected radiation was detected with an InSb photo-voltaic detector operated at liquid nitrogen temperature or a Cu doped Ge photoconductive detector at liquid helium temperature. The data were taken by sweeping magnetic field at fixed photon energies.

(c) Results

Figure 2 shows the experimental traces of reflected intensity vs. magnetic field at two photon energies. The oscillations in the upper trace are due to the transitions (B in Fig. 1)

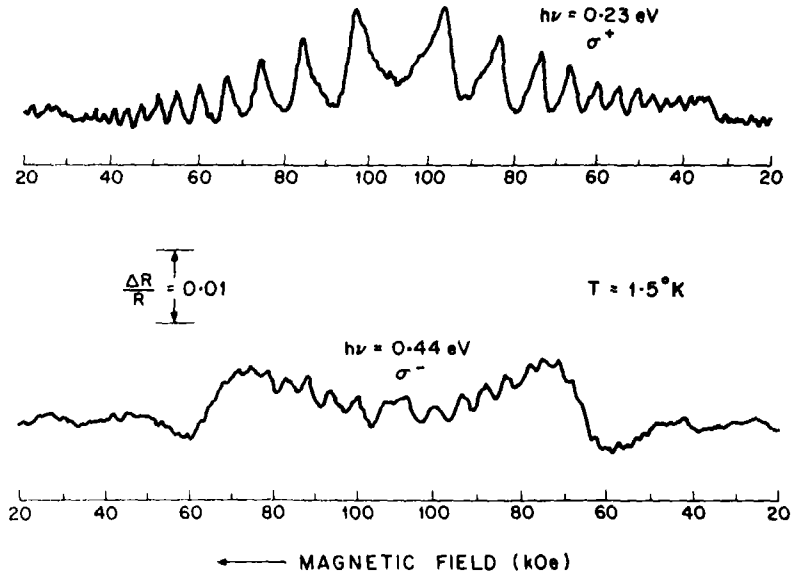


Fig. 2. Experimental traces of the magnetoreflexion made by sweeping the magnetic field at fixed photon energies. Upper traces show peaks due to the $\Gamma_8 \rightarrow \Gamma_8$ transitions, and the lower trace shows small peaks from the $\Gamma_8 \rightarrow \Gamma_8$ transitions superimposed on a large $\Gamma_7 \rightarrow \Gamma_8$ peak.

between Γ_8 bands. The lineshape, with sharp low field edge and high field tail, has the same form as the theoretical lineshape calculated from the form of the joint density of states of the magnetic subbands [17]. The large peak in the lower trace is due to a $\Gamma_7 \rightarrow \Gamma_8$ transition and the smaller oscillations are due to $\Gamma_8 \rightarrow \Gamma_8$ transitions. Figures 3 and 4 show the plots, taken from reflection maxima, of $h\nu$ vs. H for the two sets of transitions. The $\Gamma_7 \rightarrow \Gamma_8$ transitions were seen at photon energies up to 0.55 eV but are plotted only to 0.2 eV in Fig. 4 (and between 0.19 and 0.39 eV for the σ^- polarization in Fig. 6). The reflection maxima are plotted because they are the easiest to identify and because theoretically they should be very close to the resonance fields [17].

3. DISCUSSION OF RESULTS

(a) Theory

The reader is referred to Refs. [11] and [15] for a discussion of the theory which, for the

most part, has been used to generate the magnetic energy levels and the optical transition energies. Here we state several results of this theory and list the parameters which enter into the fitting process. The new aspects of our theoretical work are discussed below and in Section 3(d), and the algebraic details of this are given in Appendix B.

The coupled Hamiltonian we use has dimension 8×8 corresponding to two spin states for the Γ_8 conduction band, Γ_8 valence band, Γ_7 valence band and Γ_7 valence band. The mutual interactions between these bands are fully included, whereas the interactions of these bands with remote bands are brought in to order k^2 via effective mass parameters. The magnetic field splits each band into subbands, and the simplest solution of the coupled Hamiltonian for the n th subband of band j is

$$\psi_j^n(\mathbf{r}) = \sum_i U_{ij} f_i^n(\mathbf{r}) u_{i0}(\mathbf{r}). \quad (1)$$

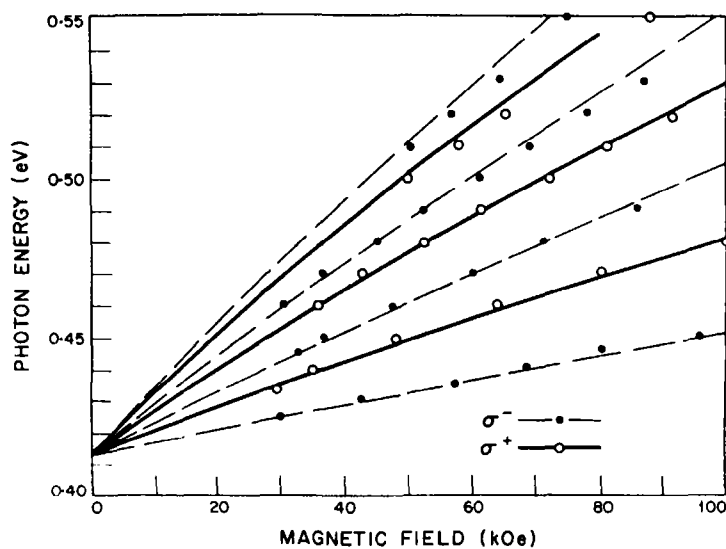


Fig. 3. The open and closed circles show the positions of the reflectivity peaks for σ^+ and σ^- polarizations due to $\Gamma_7' \rightarrow \Gamma_8'$ transitions. The solid and dashed curves give the transition energies from the theory.

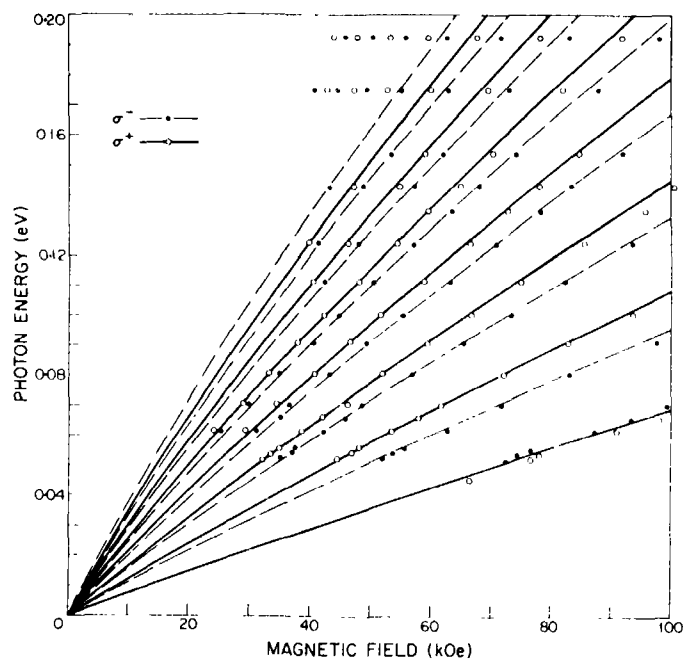


Fig. 4. $\Gamma_8' \rightarrow \Gamma_8'$ transition energies with experimental points and theoretical curves. These transitions have been seen up to 0.55 eV, and more of the spectrum is shown in Fig. 6.

The U_{ij} are elements of the unitary matrix, dependent upon H and n , which diagonalized the Hamiltonian; $f_i^n(\mathbf{r})$ contains a one dimensional harmonic oscillator function, $\phi_n^{i'}$, of order n' , where the relation between n and n' depends on i' but is independent of n (for example, $n' = n + 1$ for band i' and $n' = n - 1$ for band i''). The $u_{i0}(\mathbf{r})$ are the band-edge ($\mathbf{k} = 0$) Bloch functions for the eight bands, and transform as eigenvectors of the total angular momentum, $\mathbf{J}$, and the component along the magnetic field direction, M_J . In particular, the association is $U_2 : \mathbf{J} = \frac{1}{2}, M_J = \frac{1}{2}, U_3 : \mathbf{J} = \frac{1}{2}, M_J = -\frac{1}{2}, U_4 : \mathbf{J} = \frac{1}{2}, M_J = \frac{3}{2}, U_5 : \mathbf{J} = \frac{1}{2}, M_J = -\frac{3}{2}$.

Isotropy of the energies in the k_1k_2 plane, where k_3 is along the direction of $\mathbf{H}$, is a necessary condition for a solution in the form of equation (1). This problem has been handled in Ref.[14] by separating the k_1 and k_2 parts of the energy into an isotropic part and a remainder. The isotropic part is treated exactly and, if necessary, the remainder is included as a perturbation between particular subbands. The perturbation is proportional to

omitted. Since this interaction is of prime interest as a source of the unexplained behavior of $h\nu$ vs. $\mathbf{H}$ for the $\Gamma_8^+ \rightarrow \Gamma_8^+$ transitions at high photon energies, discussed in Section 3(d), we have developed an alternative isotropic approximation which is improved in this respect. The details of this are discussed in Appendix B.

As mentioned above, the peaks in the magnetoreflexion are predicted to be close to the onset of the interband transitions, which occurs at $k_3 = 0$. With k_3 set equal to zero the magnetic Hamiltonian factors into two 4×4 matrices with two sets of corresponding solutions. We use 'a' and 'b' as labels on the separated parts.

In considering the optical selection rules as well as the $\mathbf{k} \cdot \mathbf{p}$ interaction parameters it is useful to have the symmetry forms of the $u_{i0}(\mathbf{r})$ displayed (in the familiar forms of Refs.[13] and [16]) as well as the order of the harmonic oscillator function in f_i^n . We call the product of these functions θ_i^n , and choose the i ordering to coincide with that in Refs.[11] and [15]:

$$\left. \begin{array}{ll}
 \text{a-set} & \\
 \theta_1^n(\Gamma_8^+) = |5 \uparrow \rangle \phi_n & (J = \frac{1}{2}, M_J = \frac{1}{2}) \\
 \theta_2^n(\Gamma_8^+) = |2^{-1/2}(X + iY) \uparrow \rangle \phi_{n-1} & (\frac{3}{2}, \frac{1}{2}) \\
 \theta_3^n(\Gamma_8^+) = i[6^{-1/2}(X - iY) \uparrow + 2Z \downarrow] \phi_{n-1} & (\frac{1}{2}, -\frac{1}{2}) \\
 \theta_4^n(\Gamma_8^+) = i[3^{-1/2}(X - iY) \uparrow + Z \downarrow] \phi_{n-1} & (\frac{1}{2}, \frac{1}{2}) \\
 \text{b-set} & \\
 \theta_5^n(\Gamma_8^+) = |5 \downarrow \rangle \phi_n & (\frac{1}{2}, -\frac{1}{2}) \\
 \theta_6^n(\Gamma_8^+) = i[2^{-1/2}(X - iY) \downarrow] \phi_{n-1} & (\frac{3}{2}, -\frac{1}{2}) \\
 \theta_7^n(\Gamma_8^+) = i[6^{-1/2}(X + iY) \downarrow - 2Z \uparrow] \phi_{n-1} & (\frac{1}{2}, \frac{1}{2}) \\
 \theta_8^n(\Gamma_8^+) = i[3^{-1/2}(X + iY) \downarrow + Z \uparrow] \phi_{n-1} & (\frac{1}{2}, -\frac{1}{2})
 \end{array} \right\} \quad (2)$$

the anisotropy or warping of the Γ_8^+ bands, and this warping is large enough for α -Sn[8], to make the isotropic approximation potentially troublesome. In addition, to make the zero order Hamiltonian of Ref.[14] isotropic in the k_1k_2 plane at $k_3 = 0$, a large part of the interaction between the Γ_8^+ bands and the Γ_6^- conduction band (from the Γ_{15} band) is

The magneto-optical transition probability [18, 19] depends upon the optical momentum matrix element $\langle \phi_j^n | p_{opt} | \phi_i^n \rangle_{\text{total}}$, which can be broken down into the sum of two terms: the 'intra-band' term proportional to (in symbolic form as though equation (1) had a single term) $\langle f_j^n | p_{opt} | f_i^n \rangle_{\text{total}} \langle u_{j0} | u_{i0} \rangle_{\text{cell}}$ and an 'inter-band' term proportional to $\langle u_{j0} | p_{opt} | u_{i0} \rangle_{\text{cell}}$.

$\langle f_j^n | f_i^n \rangle_{\text{xtal}}$. For mixed bands with solutions of the form of equation (1) both types of matrix elements are nonzero for either the intraband or interband transitions. For the transitions of interest to us the 'interband' terms are much larger than the 'intraband' and are the only ones we consider.

For our work in the Faraday configuration, with the optical electric field $\perp \mathbf{H}$, we distinguish between the σ^+ polarization with matrix element $\langle \psi_i | (p_1 + ip_2) | \psi_f \rangle$ and the σ^- polarization with matrix element $\langle \psi_i | (p_1 - ip_2) | \psi_f \rangle$. The σ^+ polarization connects an initial state to final states of one unit less of angular momentum ($\Delta M_j = -1$), and σ^- connects to final states of one unit more of angular momentum ($\Delta M_j = +1$). By examination of the partial wave functions of equation (2) it is seen that initial and final states are both within the a -set or both within the b -set. Furthermore, since $\langle \phi_n | \phi_{n'} \rangle = \delta_{nn'}$, in the σ^+ polarization the final state must have one unit of n less than the initial state or $\Delta n = -1$, and for $\sigma^- \Delta n = +1$.^{*}

At $\mathbf{k} = 0$ the solutions of equation (1) reduce to a single term and the probability for the transitions B in Fig. 1 between the Γ_8^+ bands vanishes. The magnetic field causes the mixing of the Γ_7^- wavefunction into the conduction band via k_1 and k_2 $\mathbf{k} \cdot \mathbf{p}$ terms, and it is this which gives a nonzero transition probability. There are four B transitions of nearly equal strength. But, as discussed below in connection with Fig. 5, the splitting of the a - and b -set solutions of the Γ_8^+ bands is such that the four transitions group into two pairs, with each member of the pair having nearly the same transition energy and occurring in the same polarization.

The A transitions are similar to the light mass valence band to conduction band transitions in InSb, for example, but with inverted initial and final states. The broaden-

ing of the large peak in the lower trace in Fig. 2 probably is caused by lifetime broadening of the Γ_7^- states. Because this valence band is submerged, a hole created by a photon can quickly recombine with an electron scattered from the Γ_8^+ band by the creation of an optical phonon. There are four possible A transitions: $\Delta n = \pm 1$ a -set and $\Delta n = \pm 1$ b -set. Unlike the case of the $\Gamma_8^+ \rightarrow \Gamma_8^+$ transitions, these four transitions do not have equal probability. In the a -set the $\Delta n = +1(\sigma^-)$ transition predominates, and in the b -set it is the $\Delta n = -1(\sigma^+)$ transition. We observe only these strongest transitions in our experiment (Fig. 3), but this is reasonable because the others are predicted to be a factor of five or six lower in intensity. A fuller discussion of the transition strengths is given in Ref.[11].

(b) Parameters

Two types of parameters are involved in our $\mathbf{k} \cdot \mathbf{p}$ magnetic Hamiltonian. The first consists of quantities which enter into the mutual interactions of the coupled bands of Fig. 1:

$$\begin{aligned} E_0 &\equiv E(\Gamma_8^+) - E(\Gamma_7^-) \\ \Delta &\equiv E(\Gamma_8^+) - E(\Gamma_7^+) \\ E_p &\equiv 2mP^2/\hbar^2, \end{aligned} \quad (3)$$

where $P \equiv (-i\hbar/m)\langle S | p_x | X \rangle$, with m the free electron mass and p_x the x component of the momentum operator. The second consists of quantities which come from the interactions with the more remote bands; these are γ_1 , γ_2 , γ_3 , κ and q [14, 15]. The parameters κ and q multiply terms which are present only when the magnetic field is nonzero. The quantity q is nonzero only when there is a spin-orbit coupling. In the past q has been estimated to be small and assumed to be zero. Recently Pidgeon and Groves[20] found from magnetoreflexion experiments that $q = 0.4$ for InSb, and Hensel and Susuki[21] found that $q = 0.06$ for Ge from measurements of the valence-band g -factor anisotropy under uni-

^{*}Our choice here of σ^+ corresponding to $\langle \psi_i | (p_1 + ip_2) | \psi_f \rangle$ is the same as Ref.[18], for example. The opposite convention was used in Ref.[11].

axial stress. As shown in Ref. [21], q arises from the spin-orbit splitting of the Γ_{15} conduction band, Δ_{15} . It will be comparable to the other higher-band parameters when this splitting is a non-negligible fraction of the $\Gamma_{15} - \Gamma_7$ energy separation, $E_{15} - E_0$.

It is useful to show the composition of the higher band parameters in terms of the $\mathbf{k} \cdot \mathbf{p}$ contributions from bands of particular symmetries. This has been done in terms of single group symmetries [18] but we take the spin-orbit splitting of the Γ_{15} conduction band into account which gives a q contribution to each parameter [21].

$$\left. \begin{aligned} \gamma_1 &= \frac{1}{4}(F' + 2G + 2H_1 + 2H_2) + \frac{1}{2}q, \\ \gamma_2 &= \frac{1}{4}(F' + 2G - H_1 - H_2) + \frac{1}{2}q, \\ \gamma_3 &= \frac{1}{4}(F' - G + H_1 - H_2) + \frac{1}{2}q, \\ \kappa &= \frac{1}{4}(F' - G - H_1 + H_2) + \frac{1}{2}q, \end{aligned} \right\} \quad (4)$$

where

$$\begin{aligned} F' &= \frac{2}{m} \sum_i |\langle X | p_z | u_{i,0} \rangle|^2 / (E_0 - E_i), \\ G &= \frac{1}{m} \sum_i |\langle X | p_x | u_{i,0} \rangle|^2 / (E_0 - E_i), \\ H_1 &= \frac{2}{m} \sum_i |\langle X | p_y | u_{i,0} \rangle|^2 / (E_0 - E_i), \\ H_2 &= \frac{2}{m} \sum_i |\langle X | p_z | u_{i,0} \rangle|^2 / (E_0 - E_i), \\ q &= \frac{4}{9m} \sum_i |\langle X | p_y | u_{i,0} \rangle|^2 \Delta_i / (E_0 - E_i)^2, \end{aligned} \quad (5)$$

and, again, $E_0 = E(\Gamma_7')$. The sum in each expression includes all higher bands of the symmetry indicated. The quantities in equation (5) are dimensionless and must be multiplied by $\hbar^2/2m$ to equal parameters with the same symbol in the original [22] and review [16] references. The expression for q is that given in Ref [21], with Δ_i the spin-orbit splitting of the i th Γ_{15} band.

The Γ_7' valence band derives from the

single group Γ_{27}' , and the prime of F' indicates that the Γ_7' valence band is to be excluded from the sum as it is not a higher band. Thus the magnitude of F is relatively large and that of F' is very much smaller. The quantity H_2 is also expected to be small because the Γ_{25} levels, derived from atomic f functions, are thought to be far above the valence band.

(It is hoped that our use of several types of notation helps to relate this paper to many previous papers, with a minimum of confusion. The relations between the γ 's and the parameters used in Ref. [14], which we call $\bar{\gamma}$'s, are given in equation (A1). In some sections of this paper we find it desirable to isolate not only the $\Gamma_{25}' - \Gamma_2'$ interaction but also the $\Gamma_{25}' - \Gamma_{15}$ interaction. The γ^0 's are then used and these are related to the γ 's in equation (B4).)

(c) Fitting procedure and numerical results

One approach to the fitting problem, and that used for the HgTe study [11], is to generate a starting set of γ 's and κ by assuming that G and H_1 have the same values for α -Sn as for Ge ($G \approx -1$, $H_1 \approx -5$). (Actually, as shown in Ref. [8], G and H_1 can be estimated from available experimental data, namely the conduction band anisotropy [8] and the average valence band mass [23]. This will be discussed more fully below.) We can estimate q by assuming that only the lowest Γ_{15} conduction band contributes to H_1 and q , i.e.

$$q = -\frac{2}{9} H_1 \Delta_{15} / (E_{15} - E_0). \quad (6)$$

As we discuss below, estimates of Δ_{15} and E_{15} are available from band structure calculations. The energy separation E_q can be equated to the $\mathbf{H} = 0$ intercept in Fig. 3; Δ can be estimated from the 'x' rule and the splitting of the $A_3 \rightarrow A_1$ transitions seen in the reflectivity [24]; and, finally, E_p can be taken to be the same as found in InSb or Ge. This gives the required information to generate a starting set of theoretical transition energies,

which one then hopes to improve by making small changes in parameters.

At this point a comparison of the theoretical and experimental transition energies for the $\Gamma_8^+ \rightarrow \Gamma_8^+$ transitions reveals a unique and extremely useful pattern for the transitions, from which we directly determine the individual Γ_8^+ masses and, consequently, are able to simplify the entire fitting procedure. This is shown in Fig. 5. The conduction band spin splitting between *a*- and *b*- set subbands of a given *n*-value is about the same as that of the valence band. Therefore, each $\Gamma_8^+ \rightarrow \Gamma_8^+$ reflectivity peak is made up of an unresolved doublet; a σ^+ peak arising from an *a*-set σ^+

and a *b*-set σ^+ transition, with the same being true for the σ^- transitions. The photon energy difference in Fig. 4 between a σ^+ transition and the nearest σ^- transition is twice the valence band cyclotron energy, or $-2\hbar eH/(cm_i^*)$ (where $m_i^* < 0$). The energy difference between adjacent σ^+ or σ^- transitions is the usual reduced cyclotron energy, $(\hbar eH/c)((1/m_i^+) - (1/m_i^-))$. Since m_i^+ is measured from the $\sigma^+ - \sigma^-$ separation, this second spacing may be used to determine m_i^* .

We are now able to improve upon our starting values for the γ 's, κ and q . (The algebra associated with this is given in Appendix A.) We do not have enough information to specify all of these so we again make the simplifying assumptions that H_1 comes entirely from the nearest Γ_{15} conduction band and that $F' = H_2 = 0$. With the experimental values of the valence-band effective mass, conduction-band effective mass, conduction-band anisotropy, and with the use of equations (A7), (A12), (A13) and (B4) we can solve for E_p , H_1 , and q , for a given value of G . The curvature of the Γ_7^- band is caused by $\mathbf{k} \cdot \mathbf{p}$ interactions with Γ_8^+ and Γ_7^+ bands, and $m^*(\Gamma_7^-)$ can be expressed as a function of E_p , E_n and Δ . We let the remaining unknown, Δ , vary in making the fit to the transitions of Fig. 3. In summary, the direct measure of $m_i^*(\Gamma_8^+)$ from the $\Gamma_8^+ \rightarrow \Gamma_8^+$ transitions, plus the Γ_8^+ anisotropy from Ref. [8], starts us on a simple and direct fitting procedure from which the other band structure parameters are determined. To test how sensitive our parameters are to the assumptions, such as $H_2 = 0$, we repeat the process substituting in values of H_2 which are typical of the value suggested for Ge[21]. This is discussed further below.

The Γ_8^+ anisotropy of α -Sn is larger than that of Ge or InSb. As shown in the Appendix, the anisotropy or warping is proportional to $\gamma_3 - \gamma_2$ which, from equation (4) or equation (A8) is seen to be equal to $\frac{1}{2}G - \frac{1}{4}H_1 + q$. Within the approximation of equation (6).

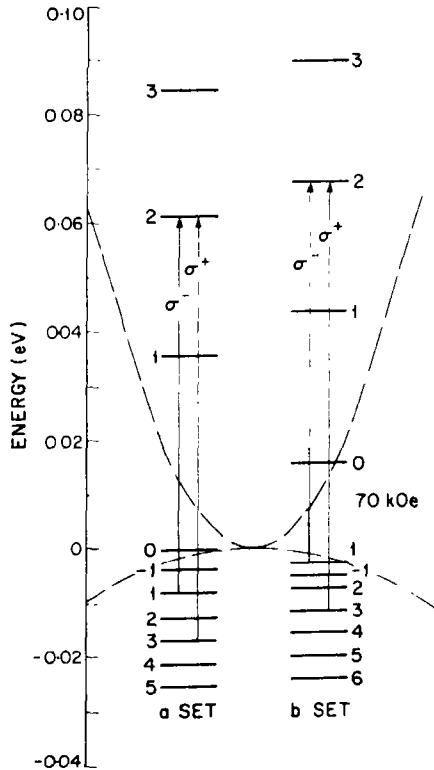


Fig. 5 The lowest Landau levels for the Γ_8^+ bands at 70 kOe. The arrows show optical transitions to the $n-2$ levels of the conduction band. The difference between the σ^+ and σ^- transition energies to a given conduction band level is a direct measure of the valence band level spacing.

this becomes $\frac{1}{2}G - \frac{1}{3}(1+3d)H_1$, where $d = 2\Delta_{15}/[9(E_{15} - E_0)]$. (Or see equation (A9) for alternative notation.) An increase in the magnitude of H_1 (and/or d) and a decrease in the magnitude of G , in comparison to the other materials, is needed. It turns out that the necessary change under the constraint $G = 0$ (i.e. the constraint that the predominant Γ_{8^+} Γ_{15} interaction in equation (5) comes from a Γ_{15} conduction band) gives a predicted m_1^* which is smaller than observed.

This problem was noted in Ref [8]. The size of the discrepancy here is less than in Ref [8] because our value of m_1^* is smaller than the value used there and because we include the effect of q , however, the problem of the sign of G remains.

The Γ_{8^+} bands for α -Sn derive largely from atomic $5p$ orbitals. The Γ_{15} bands which contribute to the $\mathbf{k} \cdot \mathbf{p}$ sum for G derive from antibonding d -like orbitals. A negative value of G would indicate that the predominant interaction is with a conduction band of $5d$ character, and a positive value of G would result if the $4d$ valence band made the larger contribution. Apparently α -Sn is the only diamond/zincblende semiconductor where there has been a question about the sign of G . Both the determination of the anisotropy and that of m_1^* for α -Sn are direct and relatively free of complications. It should be added that this problem does not arise from setting I' and H_1 equal to zero. If these parameters have nonzero and negative values G must be even larger. The mass and anisotropy values can be satisfied with negative G if q (or d) is free to vary. However, with $\Delta_{15} = 0.5$ eV, as discussed below, E_{15} must be no higher than about 1.0 eV. This is much lower than the value generated from band structure calculations which, at lowest are about 2.0 eV [25] (see Section 3(d)). However, there are other results of this experiment and the oscillatory magnetoresistance [26] which require a low value of $E(\Gamma_{15})$ if they are to be explained by the variation of E with k predicted from the $\mathbf{k} \cdot \mathbf{p}$ Hamiltonian, and we do

not rule out this explanation which retains $G < 0$. This will be discussed further in Section 3(d).

The problem of the sign of G is not particularly important for fitting the magnetoreflexion results. Within reason, a set of parameters which gives the proper masses will fit the data of Figs. 3 and 4. However, the sign and magnitude of G are important for deducing information about the Γ_{15} band from the measured masses and conduction band anisotropy. In Table 1 we first list parameters consistent with $G = 0$, which includes the low Γ_{15} band, but with Δ_{15} as calculated in Ref. [25]. To position the Γ_{15} band as calculated in Ref. [25], G must be +0.5, as shown in the second part of Table 1. The Γ_{8^+} masses are the classical (high n) cyclotron masses for the (100) plane and are calculated from equations (A10) and (A11). The Γ_{7^-} and Γ_{7^+} masses are calculated from the expressions appropriate to $k = 0$ [16]:

$$\frac{m}{m^*(\Gamma_{7^-})} = 1 + \frac{E_p}{3} \left(\frac{1}{\Delta - E_g} - \frac{2}{E_g} \right) \quad (7)$$

and

$$\frac{m}{m^*(\Gamma_{7^+})} = \frac{E_p}{3} \frac{1}{(\Delta - E_g)} - \gamma_1. \quad (8)$$

If H_2 and the higher Γ_{15} band contribution to H_1 are -0.2 (these values have been suggested for Ge [21]) the change in the γ 's is less than 10 per cent. Such variations may be thought of as the uncertainties which result when the measured quantities, Γ_{8^+} masses for example, are known exactly. The fit of theory to experiment in Figs. 3 and 4 is very sensitive to the Γ_{8^+} masses and the Γ_{7^-} valence band mass and we estimate that these quantities are known to better than ± 5 per cent. The energy separation E_g is determined from Fig. 3 to ± 1 per cent. The combined uncertainties of the Γ_{8^+} masses, E_g , and the higher-band parameters produce an uncertainty in E_p of ± 6 per cent. The worst case combinations can make Δ as large as 0.87 eV or as small as

Table 1. Parameters determined from magnetoreflexion, with conduction band anisotropy parameter, $\bar{F}$, from magnetoresistance[8]. Energies are in units of electron volts and masses in units of the free electron mass. Set 1 parameters give highest E_{15} levels consistent with $G \leq 0$. Set 2 parameters arise from using E_{15} levels from OPW computations[26] with no constraint on G . In both sets F' , H_2 and the higher Γ_{15} contributions to H_1 are set equal to zero

	$E_g = 0.413$ $m_1^* = 0.028$	$\bar{F} = 0.91$ $m_1^* = -0.195$	$m^*(\Gamma_7^-) = -0.058$
Set 1	$G = 0$ $E_v = 24.05$ $\gamma_1 = 4.28$ $E_n = 1.15$ $\Delta = 0.80$	$H_1 = -7.20$ $E_u = 6.61$ $\gamma_2 = -1.69$ $E_n = 0.65$ $m^*(\Gamma_7^+) = -0.040$	$q = 0.98$ $\gamma_3 = 1.69$ $\kappa = -3.40$
Set 2	$G = +0.56$ $E_v = 23.93$ $\gamma_1 = 4.19$ $E_n = 2.48$ $\Delta = 0.80$	$H_1 = -8.04$ $E_u = 18.38$ $\gamma_2 = -1.73$ $E_n = 1.98$ $m^*(\Gamma_7^+) = -0.041$	$q = 0.42$ $\gamma_3 = 1.64$ $\kappa = -2.18$

0.76 eV. The Γ_7^+ mass for worst case combinations is $-0.048m$ and $-0.036m$.

The lowest σ^- transition in Fig. 4 is at too high an energy to be part of the Landau level transitions shown in Fig. 5. Our suspicion is that it is a transition from an impurity ground state associated with the $n=0$ conduction band Landau level to an excited impurity state associated with, and lying below, the $n=2$ conduction subband. The observation of impurity transitions similar to this in p -type InSb and Ge[25] makes this plausible from an experimental point of view. Evidence has been presented recently for discrete impurity levels in α -Sn under uniaxial stress which causes the splitting of the Γ_8^+ bands[9]. It would not be surprising if a similar effect were caused by a high magnetic field. Further work on the low photon energy magnetoreflexion using the 28μ line from a water vapor laser is planned. Some additional thoughts on the impurity transitions are presented in Section 3(f).

(d) Γ_{15} Band nonparabolic correction

In Fig. 6 we show the extension of the $\Gamma_8^+ \rightarrow \Gamma_8^+$ transitions to higher photon energies (for the σ^- polarization). It is seen

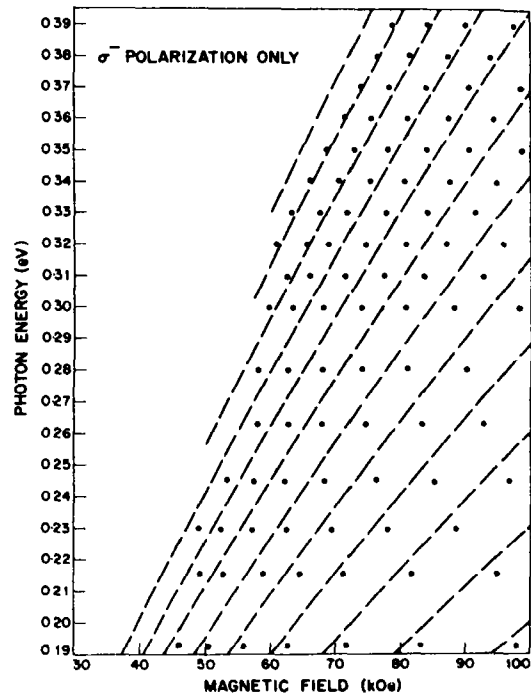


Fig. 6. A higher energy segment of the spectrum of $\Gamma_8^+ \rightarrow \Gamma_8^+$ transitions. The dots are the experimental points and the dashes give the theoretical curves. The σ^+ data and theory have been omitted to simplify the figure

from this figure, as well as from the high photon energy range in Fig. 4, that the theory predicts transition energies which are too high. Since at these photon energies the initial and final states are well into the bands, it seems reasonable that terms of higher order than k^2 from the Γ_{15} band interaction could cause the discrepancy between theory and experiment.

The parameter H_1 , again within the approximation that only the lowest Γ_{15} conduction band contributes to the sum over Γ_{15} bands, has the form

$$H_1 = E_0/[E_0 - E_{15}(0)] \quad (9)$$

with $E_0 = (2/m)(\langle X|p_q|z\rangle)^2$ as seen from equation (5), and $E_0 = E(\Gamma_8')$. More precisely, the quantity which enters the Hamiltonian is

$$H_1 = E_0/[E(\mathbf{k}) - E_{15}(\mathbf{k})], \quad (10)$$

where $E(\mathbf{k})$ is an eigenvalue of the coupled Hamiltonian. Because of the k dependence in the energy denominator of equation (10), the k^2 theory (equation (9)) will tend to give Γ_8' conduction and valence band energies which are too large in magnitude. Thus qualitatively the higher order Γ_{15} terms will tend to correct the discrepancy in Figs. 4 and 6. Similar arguments apply for q , the other Γ_{15} parameter.

To test this idea quantitatively we have included the Γ_{15} bands in the magnetic Hamiltonian; i.e. increasing the size of our Hamiltonian from four to seven coupled bands (a - and b -set each containing seven eigenvalues). The algebraic details of this are given in Appendix B.

Recent OPW calculations for α -Sn[25] give the $\Gamma_8^- - \Gamma_8'$ separation as 2.43 eV and the $\Gamma_6^- - \Gamma_8'$ separation as 1.95 eV, where Γ_8^- and Γ_6^- are the double group representations of Γ_{15} and are split by a spin-orbit energy, Δ_{15} . When we use the OPW values in the full Hamiltonian we find an insignificant change in

the theoretical curves in Fig. 6. (Actually, the two transition energies for each polarization predicted from the 4-coupled band theory, which are averaged in Figs. 4 and 6, are split by an unreasonable amount at high photon energies—i.e. by an amount which should make them individually observable. This is due to a rapid change in conduction band g -factor, from large negative to large positive, predicted by the 4-coupled band theory. The main effect of coupling in the Γ_{15} bands is to give a slower variation to the g -factor and thus give pairs of transition energies which are close in energy, even at $h\nu \approx 0.6$ eV, as is observed experimentally. See Appendix B for further discussion.) We have tried decreasing the energies of the Γ_{15} bands by moderate amounts, but without success in noticeably improving the overall fit in Figs. 4 and 6.

At this point we digress to consider an interesting anomaly in the dependence of the conduction band effective mass upon electron density, or n -type doping, reported by Booth and Ewald[26] from oscillatory magneto-resistance measurements. At donor concentrations below $5 \times 10^{17} \text{ cm}^{-3}$ the conduction band mass increases with concentration (or k) in a manner predicted from the coupled $\Gamma_7^- - \Gamma_8'^+ - \Gamma_7^-$ band theory. However, in the range of $5 \times 10^{17} - 1 \times 10^{19} \text{ donors/cm}^3$ (the highest doping used in Ref.[26]) the mass increases much more rapidly than predicted by theory. This anomaly occurs at about the doping that is required to bring the Fermi level to the energy of the L_6^+ minima (see Fig. 1), and the L_6^+ electrons, through screening effects, have a pronounced effect upon the mobility of the Γ_8^+ electrons[28]. The close proximity of the Fermi level to the L_6^+ band minima may account for the anomalous mass dependence, although no mechanism for this has been found. Alternatively, the more rapid increase in mass with k may arise from a sudden change of $E(\mathbf{k})$.

To follow this further, consider the band structure shown in Fig. 7. The Γ_6^- band, from the spin-orbit split Γ_{15} band, is close enough

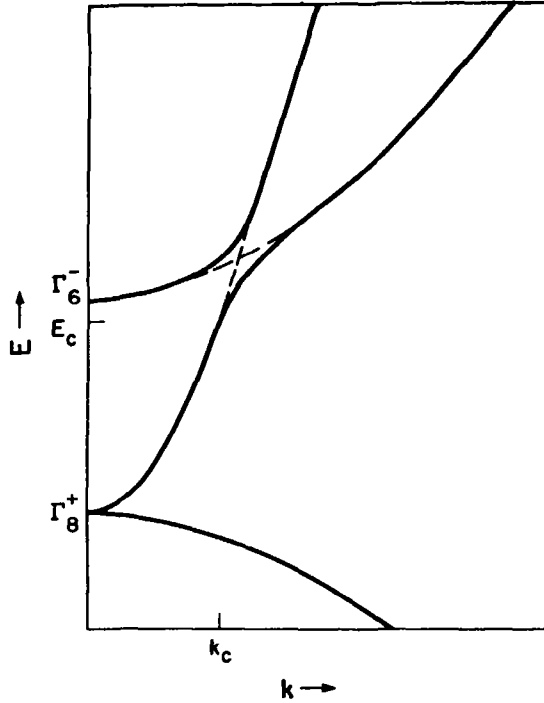


Fig. 7. A speculative modification of the band structure of Fig. 1 which qualitatively accounts for the anomalous features of the magnetoreflexion and magnetoresistance discussed in the text. In this k_c corresponds to the Fermi radius of a sphere holding $\approx 5 \times 10^{17}$ electrons/cm³ and $E_c \approx 0.1$ eV.

to Γ_8^+ , and of sufficiently large mass, that a crossing of Γ_8^+ and Γ_6^- bands would occur within the region of k -space sampled by the oscillatory magnetoresistance and magnetoreflexion experiments if there were not a weak repulsion between the bands. Although the bands do not cross the admixture of Γ_7^- wavefunction in the Γ_8^+ conduction band transfers to the upper band for $k > k_c$, and at high photon energies the electron is excited to the high band.

There are three attractive features to this band structure. First, we find that it is possible to get a good theoretical fit to the high photon energy part of the $\Gamma_8^+ \rightarrow \Gamma_8^+$ transition spectrum. Secondly, the theory incorporates a break in the effective mass vs. k behavior

as is desirable for the explanation of the experiment in Ref.[26]. Finally, the position of the Γ_{15} levels can be made low enough so the warping and valence band effective mass are compatible with $G < 0$.

On the other hand, there is no direct evidence for the band structure of Fig. 7. With a sufficiently close mesh of experimental points effects of the band crossing, such as extra transitions, strong H -dependent intensities, and anomalous $h\nu$ vs. H behavior should be seen. There is no evidence of these in our magnetoreflexion data, but a fairly large interval between photon energies was used. Magnetoresistance oscillations from both conduction bands might be seen; however, the only evidence is an unexplained beat in the oscillation magnitude for a 1×10^{19} donor/cm³ sample. Other observations are in good agreement with the band structure of Fig. 1: they do not need the low Γ_6^- band of Fig. 7 and it is hard to tell whether they are compatible or incompatible with it. Thus we must consider the band structure of Fig. 7 as highly speculative. It is in qualitative agreement with several experimental features and should be kept in mind in planning and interpreting future experiments.

If the band structure of Fig. 7 is not applicable to α -Sn then one must look to another explanations for the anomalous behavior in Figs. 4 and 6. For example, the transformation of the $k \cdot p$ Hamiltonian into a magnetic-field-effective mass Hamiltonian involves several steps in which k is assumed to be small; relativistic and many electron formulations add terms, estimated in the literature to be small, of different k dependences than those we have considered. We shall not investigate these possibilities, but only stress that, in this case, the magnetoreflexion data is not fully explained by the $k \cdot p$ theory, and this apparently is a unique situation for the diamond-zincblende lattice semiconductors[16].

(e) $E(\Gamma_8^+) - E(\Gamma_7^-)$ temperature dependence

The $\Gamma_7^- \rightarrow \Gamma_8^+$ oscillatory magnetoreflexion

tion has been measured at 1.5°, 20° and 85°K, with no observable shift in resonant energies. This is in marked contrast to the HgTe results which show large shifts over this temperature range [12]. HgTe and the $\text{Cd}_{1-x}\text{Hg}_x\text{Te}$ alloys, however, are quite different in this behavior from InSb and Ge, for example. A plot of the 0–100°K temperature dependence of $|E(\Gamma_8^+) - E(\Gamma_7^-)|$ for Ge, InSb, HgTe and α -Sn is shown in Fig. 8. This figure is presented for two reasons: first, the HgTe and α -Sn curves have not been published previously; second, the collection of different temperature dependences in Fig. 8 (and, one might add the behavior of the $\text{Cd}_{1-x}\text{Hg}_x\text{Te}$ alloys as well [27]) present a considerable challenge to any theory of temperature dependences.

(f) Comparison with other experiments

In Sections 3(c) and 3(d) we discussed the conduction band anisotropy measurements and the effective mass vs. concentration

measurements from the oscillatory magnetoresistance. A comparison of the band-edge conduction band mass values from that experiment can be made with our results, as can intraband measurements of the Γ_8^+ valence band mass.

The band edge mass for the (100) cyclotron mass from Ref. [26] is $m_c^* = 0.023m$, while we find $m_c^* = 0.028m$. This 20 per cent difference is outside the experimental error of these determinations of mass. The Γ_8^+ valence band density-of-states mass has been measured by Wagner and Ewald [23] from the free carrier reflectivity to be $0.26m$. The density-of-states mass is close enough to the (100) mass to permit a direct comparison with our value of $0.195m$.

These discrepancies between masses determined from interband and intraband experiments may be characteristic of a more general situation. For example, recent interband measurements on InSb have been analyzed to

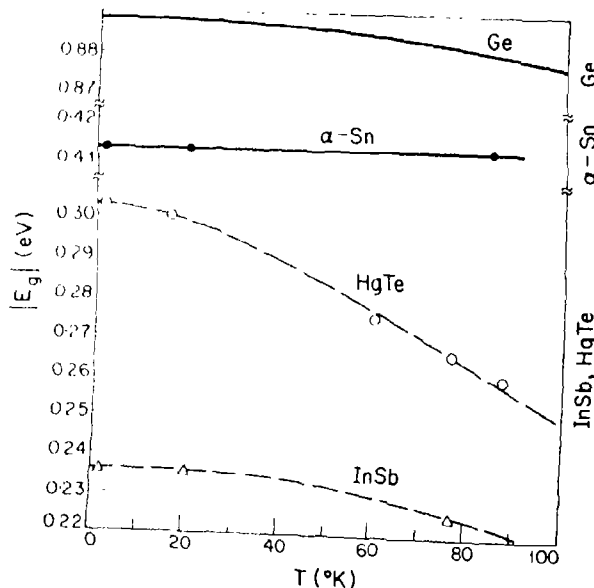


Fig. 8. A comparison of the $k = 0$ energy separation as a function of temperature for several diamond-zincblende materials. For Ge and α -Sn $|E_g|$ is $|E(\Gamma_7^-) - E(\Gamma_8^+)|$, and for InSb and HgTe it is $|E(\Gamma_6^-) - E(\Gamma_8^+)|$.

give the individual masses[20], with the result that the conduction band mass (Γ_6 band, which corresponds to our Γ_7^- band) is heavier than determined by cyclotron resonance[30] and the heavy Γ_8^+ mass is lighter than the corresponding cyclotron resonance mass [31–34]. These differences between masses determined from interband and intraband experiments have not been explained.

One possibility for resolving the mass discrepancy for α -Sn involves a different interpretation of the B transitions in Fig. 1, which we have associated with $\Gamma_8^+ \rightarrow \Gamma_8^+$ interband transitions. One might interpret these transitions as being from an impurity ground state, near $E(\Gamma_8^+)$, to excited impurity states lying slightly below each conduction band Landau level. Such transitions have been seen in magnetoabsorption measurements by Boyle[35] in n -type Ge and by Kaplan[27] in p -type Ge and InSb. If we use a band-edge mass of $m_c^* = 0.023m$ ($E_p = 27.0$ eV) and compare the positions of the conduction band levels to the transition energies in Fig. 4 we get reasonable agreement. If the spin-orbit splitting, Δ , is 0.71 eV, the agreement between theory and experiment for the $\Gamma_7^- \rightarrow \Gamma_8^+$ transitions is about as shown in Fig. 3. The discrepancies in Fig. 6 remain the same. Unfortunately the theory of the impurity transitions is so crude that it is hard to make reliable estimates of transition probabilities. However, for two reasons we believe that we are observing band-to-band transitions rather than impurity transitions. First, we can calculate the intensity of the interband transitions, and the calculated intensity is of the same order of magnitude as the observed intensity. Thus, if the B transitions are indeed impurity transitions we should observe the interband transitions as well. This cannot be correct because any additional transitions in the magnetoreflexion spectrum are at least an order of magnitude down in strength. Secondly, the B transitions we measure are of the same strength at 1.5°, 20° and 80°K. The intensity

of impurity transitions should be proportional to the occupation of the ground state, and the number of electrons in the ground state must fall rapidly between 1.5° and 20°K – or at least 80°K – as the electrons gain the thermal energy to populate the lowest conduction band levels.

Thus, we believe the discrepancy in masses remains. This is a problem which deserves additional experimental and theoretical study [36]. A question which we hope to settle in the near future by cyclotron resonance measurements is whether the intraband masses agree, i.e. masses determined by cyclotron resonance and by oscillatory magnetoresistance.

4. CONCLUSION

In summary, we have found that the magnetoreflexion results are well explained by the band structure of Fig. 1. The $\Gamma_8^+ - \Gamma_7^-$ energy separation has been determined directly from the $H = 0$ intercept of one set of transitions. The valence-band effective mass has been measured from the second set of transitions, and from this the masses $m_c^*(\Gamma_8^+)$ and $m_v^*(\Gamma_7^-)$ have been found. The quantities E_p and Δ have been deduced from the masses. Several interesting questions have arisen from this and other recent experiments: Are the deviations of theory from experiment at high photon energies for the $\Gamma_8^+ \rightarrow \Gamma_8^+$ transitions and the unexpected behavior of effective mass vs. donor concentration from oscillatory magnetoresistance measurements a result of a near crossing of Γ_6^- and Γ_8^+ conduction bands? Is this also the answer to the G problem, or is G positive, indicating a high Γ_{12}' valence band? Finally, what is the source of the discrepancy found for α -Sn and InSb between the interband and intraband masses?

Acknowledgements – It is a pleasure to acknowledge many helpful suggestions given on the theoretical parts of this paper by G. Dresselhaus, J. Casters and J. McNally provided technical assistance with the experiments. Finally, we have benefited from the many magneto-optical studies at the Francis Bitter National Magnet

Laboratory and Lincoln Laboratory, and discussions of these with K. Button, B. Lax and J. Mavroides

REFERENCES

1. BUSCH G. and KERN R., *Solid State Physics* (Edited by I. Seitz and D. Turnbull) Vol. 11, p. 1. Academic Press, New York (1960).
2. EWALD A. W. and LUTHEO N., *J. appl. Phys.* **29**, 1007 (1958).
3. EWALD A. W., *Helv. phys. Acta* **41**, 795 (1968).
4. GROVES S. H. and PAUL W., *Phys. Rev. Lett.* **11**, 194 (1963); GROVES S. H. and PAUL W., *Proc. 7th Int. Conf. Phys. Semiconductors, Paris*, p. 41. Dunod Cie. Paris (1964).
5. LUTHEO N. and EWALD A. W., *Phys. Rev.* **122**, 1431 (1961).
6. LAVINE C. E. and EWALD A. W., *Bull. Am. phys. Soc.* **11**, 847 (1966); LAVINE C. E., Ph.D. Thesis, Northwestern University (unpublished) (1968).
7. HINKLEY D. and EWALD A. W., *Phys. Rev.* **134**, A1261 (1964).
8. BOOTH B. L. and EWALD A. W., *Phys. Rev.* **168**, 805 (1968).
9. ROMAN B. L. and EWALD A. W., *Bull. Am. phys. Soc.* **13**, 408 (1968); ROMAN B. L., Ph.D. Thesis, Northwestern University (unpublished) (1968).
10. GROVES S. H., PIDGON C. R., EWALD A. W. and WAGNER R. J., *Bull. Am. phys. Soc.* **13**, 429 (1968); and *Proc. 9th Int. Conf. Phys. Semiconductors, Moscow*, p. 43. Nauka, Leningrad (1968).
11. GROVES S. H., BROWN R. N. and PIDGON C. R., *Phys. Rev.* **161**, 779 (1967).
12. PIDGON C. R. and GROVES S. H., *Proc. II-VI Semiconducting Compounds 1967 Int. Conf.* (Edited by D. G. Thomas), p. 1080. Benjamin, New York (1967).
13. LUTTINGER J. M. and KOHN W., *Phys. Rev.* **97**, 869 (1955).
14. LUTTINGER J. M., *Phys. Rev.* **102**, 1030 (1956).
15. PIDGON C. R. and BROWN R. N., *Phys. Rev.* **146**, 878 (1966).
16. KANE E. O., *The $k \cdot p$ Method: Physics of III-V Compounds* (Edited by R. K. Willardson and A. C. Beer), Vol. 1. Academic Press, New York (1966); KANE E. O., *J. Phys. Chem. Solids* **1**, 249 (1957).
17. DRESSERHAUS M. S. and DRESSERHAUS G., *Phys. Rev.* **125**, 499 (1962).
18. ROTH L. M., LAX B. and ZWEIFLING S., *Phys. Rev.* **114**, 90 (1959).
19. BURSTEIN E., PICUS G. S., WALTIS R. F. and BLATTI., *Phys. Rev.* **113**, 15 (1959).
20. PIDGON C. R. and GROVES S. H., *Phys. Rev.* **186**, 824 (1969).
21. HINSEY J. C. and SUZUKI K., *Phys. Rev. Lett.* **22**, 838 (1969).
22. DRESSERHAUS G., KIP A. F. and KLEIN C., *Phys. Rev.* **98**, 368 (1955).
23. WAGNER R. J. and EWALD A. W., *Bull. Am. phys. Soc.* **11**, 328 (1966); WAGNER R. J., Ph.D. Thesis, Northwestern University (unpublished) (1967).
24. CARDONA M. and GREENAWAY D. J., *Phys. Rev.* **125**, 1291 (1962).
25. VAN DYKE J. P. and HERMAN F., *Bull. Am. phys. Soc.* **13**, 413 (1968); POLLAK F. H., CARDONA M., HIGGINBOTHAM C. W., HERMAN F. and VAN DYKE J. P., to be published in *Phys. Rev.*; see also the pseudopotential calculations of S. Bloom and T. K. Bergstresser, *Solid State Commun.* **6**, 465 (1968).
26. BOOTH B. L. and EWALD A. W., *Phys. Rev.* **168**, 796 (1968).
27. KAPLAN R., *Phys. Rev. Lett.* **20**, 329 (1968).
28. BOOTH B. L. and EWALD A. W., *Phys. Rev. Lett.* **18**, 491 (1967).
29. SCOTT M. W., *Bull. Am. phys. Soc.* **14**, 416 (1969); see also Ref.[12] for additional discussion and references.
30. DICKLY D. H. and JOHNSON E. J., *Bull. Am. phys. Soc.* **13**, 430 (1968); and JOHNSON E. J. and DICKLY D. H., (to be published in *Phys. Rev. B*).
31. BAGGLEY D. M. S., ROBINSON M. L. and STRADING R. A., *Phys. Lett.* **6**, 143 (1963).
32. LOHYER H. I. and ASCARFELLI G., *Proc. 9th Int. Conf. Phys. Semiconductors, Moscow*, p. 326. Nauka, Leningrad (1968).
33. BUTTON K. J., LAX B. and BRADLEY C. C., *Phys. Rev. Lett.* **21**, 350 (1968).
34. BRICHER A., LAX B. and BUTTON K. J., *Bull. Am. phys. Soc.* **14**, 433 (1969).
35. BOYLE F. W. S., *J. Phys. Chem. Solids* **8**, 270 (1959).
36. We have ignored the effects of excitons in this study because of the lack of experimental and theoretical information about them for the 'inverted' band structure. The exciton effects in InSb are better understood, but do not account for the mass discrepancies in that material.
37. See e.g. LOWDEN P., *J. Chem. Phys.* **19**, 1396 (1951).

APPENDIX A

There are several analytic approximations to the Γ_7^- , Γ_7^+ , Γ_7^- coupled $\mathbf{k} \cdot \mathbf{p}$ matrix Hamiltonian. For example, the $E(\mathbf{k})$ dispersion relations for the Γ_7^+ bands of Ref.[22] are exact to order k^2 but do not include the nonparabolicity resulting from the strong coupling to the Γ_7^- band. Perturbation expressions are given in Ref.[16] which include the nonparabolicity of the 'light' Γ_7^+ band but are approximations to the correct k^2 angular dependence. Reference[14] gives the magnetic field solution to the problem of Ref.[22]. The effective mass parameters in that case are $\tilde{\gamma}_1$, $\tilde{\gamma}_2$, $\tilde{\gamma}_3$ and $\tilde{\kappa}$. These are given by equation (4) if the quantity I is substituted for F' , or

$$\begin{aligned}\tilde{\gamma}_1 &= \gamma_1 - \delta \\ \tilde{\gamma}_2 &= \gamma_2 - \delta/2 \\ \tilde{\gamma}_3 &= \gamma_3 - \delta/2 \\ \tilde{\kappa} &= \kappa - \delta/2,\end{aligned}\tag{A1}$$

where $\delta \equiv E_v/(3E_g)$ with E_v and E_g defined in equation (3). For α -Sn δ is about 20.

Our fitting is done with the γ 's as the remote band parameters, or alternatively with G and H_1 of equation (5). However, we make use of a warping parameter from Ref.[8] which is defined in the notation of Ref.[22], and

we use expressions for the Γ_8^+ band (100) cyclotron masses written in the notation of Ref.[14]. In this Appendix we re-express the warping and the Γ_8^+ masses and give the algebra for the fitting procedure described in Section 3(c).

The expression for Γ_8^+ energies from Ref.[22] is

$$E = \frac{\hbar^2}{2m} \left[Ak^2 \pm Bk^2 \left(1 + \frac{C^2}{B^2} f \right)^{1/2} \right], \quad (\text{A2})$$

where

$$f = (k_x^2 k_y^2 + k_y^2 k_z^2 + k_z^2 k_x^2) / k^4. \quad (\text{A3})$$

The plus sign applies for the conduction band and the minus sign for the valence band. The effective mass parameters A , B and C can be expressed in terms of those of equation (A1):

$$\begin{aligned} A &= -\bar{\gamma}_1 \\ B &= -2\bar{\gamma}_2 \\ C^2 &= 3[(2\bar{\gamma}_3)^2 - (2\bar{\gamma}_2)^2]. \end{aligned} \quad (\text{A4})$$

The conduction-band anisotropy parameter defined in Ref.[8] is

$$\bar{F} = -C^2/[B(A+B)], \quad (\text{A5})$$

which can be written in terms of the parameters of equation (A1):

$$\bar{F} = -\frac{6(\bar{\gamma}_1 - \bar{\gamma}_2)(\bar{\gamma}_3 + \bar{\gamma}_2)}{\bar{\gamma}_2(\bar{\gamma}_1 + 2\bar{\gamma}_2)} \quad (\text{A6})$$

$$= -\frac{6(\gamma_1 - \gamma_2)[1 - (\gamma_1 + \gamma_2)/\delta]}{\delta(1 - 2\gamma_2/\delta)[1 - (\gamma_1 + 2\gamma_2)/(2\delta)]} \quad (\text{A7})$$

where the form of equation (A7) is motivated by the fact that δ is about an order of magnitude larger than the γ 's. $\bar{F}$ is predominantly determined by the quantity $(\gamma_1 - \gamma_2)/\delta$, and, from equation (4), $\gamma_1 - \gamma_2$ is

$$(\gamma_1 - \gamma_2) = \frac{1}{2}G - \frac{1}{2}H_1 + q. \quad (\text{A8})$$

A more transparent form of this quantity comes from equation (B4) where the Γ_{15} band contributions are written explicitly:

$$\gamma_3 - \gamma_2 = \frac{1}{2}G + \frac{E_q}{3E(\Gamma_8^-)}. \quad (\text{A9})$$

which shows that it is the Γ_8^- band which is important for the warping. (The zero of energy has been taken at $E(\Gamma_8^+)$, i.e. $E(\Gamma_8^-)$ is the energy of Γ_8^- above Γ_8^+ .)

Although we do not have exact expressions for the Γ_8^+ cyclotron masses for the (100) plane, approximate expressions can be found, as discussed in Appendix B, which are:

$$(m/m_e^*)_{(100)} = (-\bar{\gamma}_1 - 2\bar{\gamma}_2) \sqrt{1 - \bar{F}/8} \quad (\text{A10})$$

and

$$(m/m_e^*)_{(100)} = -\bar{\gamma}_1 + \bar{\gamma}_2 - \frac{1}{2}\sqrt{\bar{\gamma}_2^2 + 3\bar{\gamma}_3^2}. \quad (\text{A11})$$

With the simplification that H_2 and F are zero and that only one Γ_8 band contributes to the γ 's, these become:

$$(1 - \bar{F}/8)^{1/2} (m/m_e^*) = 1 + 2\delta - \frac{E_q}{3E(\Gamma_8^-)} + \frac{4}{3}G, \quad (\text{A12})$$

and

$$(m/m_e^*) = 1 - \frac{E_q}{3E(\Gamma_8^-)} - \frac{5}{12} \frac{E_q}{E(\Gamma_8^-)} + \frac{3}{8}G. \quad (\text{A13})$$

where we have used equation (B4) and, again, $\delta = E_p/(3E_q)$. If we regard the quantities on the left-hand side of equations (A7), (A12) and (A13) as determined by experiment we have three equations relating the quantities E_p , E_q , $E(\Gamma_8^-)$, $E(\Gamma_8^+)$ and G . If we use the OPW computation[26] result $E(\Gamma_8^-) - E(\Gamma_8^+) = 0.5$ eV, and set $G = 0$ we get the first set of parameters given in Table 1. To preserve the other OPW computation result that $E(\Gamma_8^+) = 2.4$ eV, we find that G must be $+0.5$, as shown in the second part of Table 1.

APPENDIX B

In this section we outline some of the algebra which is useful if the Γ_{15} band (Γ_8^+ and Γ_8^- with spin-orbit coupling) is to be treated explicitly. This may be done for the coupled $\Gamma_7^- - \Gamma_8^+ - \Gamma_7^+$ Hamiltonian which in lowest order contains Γ_{15} effects in terms varying as k^2 and can be made more exact by a perturbation procedure. Or the Γ_8^- and Γ_8^+ bands can be treated on an equal basis with the others by expanding the dimension of the $\mathbf{k} \cdot \mathbf{p}$ matrix Hamiltonian from 4×4 to 7×7 .

To improve the 4×4 Hamiltonian we seek the expressions which show the Γ_{15} band contributions to the γ 's, κ and q ; essentially Equation (4) but with explicit Γ_8^- and Γ_8^+ parts. These can be found by comparing terms in two Hamiltonians. The first is the Γ_8^+ Hamiltonian of Luttinger[14], written in the most general form for Γ_8^+ symmetry with the γ 's, κ and q as parameters. The second is the $\mathbf{k} \cdot \mathbf{p}$ Hamiltonian for the Γ_8^+ bands which has been expanded to order k^2 with coefficients in the form of the quantities on the right-hand side of equation (5). An alternative method, which we shall use, is to write out the 7×7 matrix Hamiltonian and then contract this to dimension 4×4 . In this process we obtain the expressions desired.

The following basis functions, $u_n(\mathbf{r})$, are added to those of equation (2):

$$\begin{aligned} \text{a-set} \\ u(\Gamma_8^+) &= \left\{ \left(\frac{1}{2} \right)^{1/2} \left\{ (x + iy) \downarrow - 2z \uparrow \right\} \right\} & (\mathbf{J} = \frac{1}{2}, M_z = \frac{1}{2}) \\ u(\Gamma_8^-) &= \left\{ \left(\frac{1}{2} \right)^{1/2} (x - iy) \downarrow \right\} & (\frac{1}{2}, -\frac{1}{2}) \\ u(\Gamma_8^+) &= \left\{ \left(\frac{1}{2} \right)^{1/2} \left\{ (x + iy) \downarrow + z \uparrow \right\} \right\} & (\frac{1}{2}, \frac{1}{2}) \\ \text{b-set} \\ u(\Gamma_8^-) &\approx \left\{ \left(\frac{1}{2} \right)^{1/2} (x + iy) \uparrow \right\} & (\frac{1}{2}, \frac{1}{2}) \\ u(\Gamma_8^+) &= \left\{ \left(\frac{1}{2} \right)^{1/2} \left\{ (x - iy) \uparrow + 2z \downarrow \right\} \right\} & (\frac{1}{2}, -\frac{1}{2}) \\ u(\Gamma_8^-) &= \left\{ \left(\frac{1}{2} \right)^{1/2} (x - iy) \uparrow - z \downarrow \right\} & (\frac{1}{2}, -\frac{1}{2}) \end{aligned} \quad (\text{B1})$$

The quantity $\mathbf{r}$ transforms as the vector component and the quantity X , in equation (2), transforms as the product of vector components v_z .

We order the basis vectors for each set as they appear in equation (B1) for the first three, and then as they appear

in equation (2) for the remainder. When k_z is set equal to zero the a - and b -sets are not coupled, and the eigenvalues and eigenvectors are found by diagonalizing two 7×7 matrices. We illustrate this for the a set matrix Hamiltonian.

$$\mathcal{H}_a = \begin{pmatrix} \mathcal{H}_1 & \mathcal{H}_2 \\ \mathcal{H}_3 & \mathcal{H}_4 \end{pmatrix}$$

where

$$\mathcal{H}_1 = \begin{pmatrix} L_{\kappa} + \epsilon[1 - (\gamma_1/6)]k^2 & -(\epsilon\gamma_1/2\sqrt{3})k^2 & -(\epsilon\gamma_1/2\sqrt{3})k^2 \\ (1, 2)^+ & E_{\kappa} + \epsilon[1 - (\gamma_1/2)]k^2 & (\epsilon\gamma_1/\sqrt{6})k^2 \\ (1, 3)^+ & (2, 3)^+ & L_{\kappa} + \epsilon[1 - (\gamma_1/3)]k^2 \end{pmatrix}$$

$$\mathcal{H}_2 = \begin{pmatrix} 0 & (Q/\sqrt{3})k & 0 & (Q/\sqrt{2})k \\ 0 & 0 & (Q/\sqrt{3})k & -(Q/\sqrt{6})k \\ 0 & (Q/\sqrt{6})k & (Q/\sqrt{2})k & 0 \end{pmatrix} \quad (\text{B2})$$

and

$$\mathcal{H}_3 = \begin{pmatrix} L_{\kappa} + \epsilon k^2 & (P/\sqrt{2})k & (P/\sqrt{6})k & (P/\sqrt{3})k \\ (1, 2)^+ & \epsilon(1 - \gamma_1^0 - \gamma_2^0)k & \epsilon\sqrt{3}\gamma_4^0 k^2 & \epsilon\sqrt{2}\gamma_4^0 k^2 \\ (1, 3)^+ & (2, 3)^+ & \epsilon(1 - \gamma_1^0 + \gamma_2^0)k^2 & \epsilon\sqrt{2}\gamma_2^0 k^2 \\ (1, 4)^+ & (2, 4)^+ & (3, 4)^+ & \Delta + \epsilon(1 - \gamma_1^0)k^2 \end{pmatrix}.$$

The following notation is used in equation (B2): $L_{\kappa} = E(1, 1) + E_{\kappa} - E(1, \kappa^+)$ and $E(1, \kappa^+) = 0$, $\epsilon = \hbar^2/(2m)$, $k^2 = k_x^2 + k_y^2$, $k_{\pm} = k_x \pm ik_y$, $k_{\pm}^{\pm} = ik_{\pm}$, $Q = (\hbar/m)(\chi|p_x|z)$, $P = (\hbar/m)(\chi|p_x|Y)$, $\gamma_1 = (2/m)(\chi|p_x|z)^2/[L(1, 1) - E(1, 1)]$, $\gamma_1^0 = \gamma_1^0 + \gamma_2^0$, $\gamma_2^0 = \gamma_1^0 - \gamma_2^0$. We have included the interaction of the Γ_1 conduction band with the Γ_{15} bands to order k^2 through the parameter γ_1 , because OPW calculations [26] place the Γ_1 band within several electron volts of the Γ_{15} bands, and the matrix element between them is of the same order of magnitude as that between the Γ_{15} and Γ_{15} bands (represented by P or E_p). The quantity $|\chi\rangle$ is a basis vector of Γ_1 , transforming as a bonding s -like function. The interactions with the Γ_{15} , Γ_1 and higher Γ_{15} bands are represented by the quantities γ_1^0 , γ_2^0 , γ_3^0 and κ^0 , where these quantities are defined by equation (4) if the contributions from the lowest Γ_{15} conduction band are omitted, as well as the free electron contribution to γ_1 and κ .

The 7×7 matrix of equation (B2) can be contracted into 4×4 form using the relationship [37]

$$\mathcal{H}_{aa} = \mathcal{H}_{aa}^* + \sum_n \mathcal{H}_{an} \mathcal{H}_{na} / (E - E_n) \quad (\text{B3})$$

where $\mathcal{H}^*$ is the 4×4 matrix $\mathcal{H}_{aa}$, the summation is over Γ_{15} bands, and E is the eigenvalue of the 4×4 Hamiltonian. By dropping the higher order terms in equation (B3) we neglect the effects of the Γ_1 bands on the Γ_{15} , Γ_2^- and γ_7 bands through the Γ_1 bands. If we replace E by $E(\Gamma_{15}^+)$, which is taken as zero, and compare terms with Luttinger's matrix Hamiltonian (essentially the (2, 2), (2, 3) and (3, 3) terms of $\mathcal{H}_a$) we find:

$$\gamma_1 = \gamma_1^0 - 1 + \frac{E_q}{3} \left[\frac{1}{E_{\kappa}} + \frac{1}{E_n} \right]$$

$$\gamma_2 = \gamma_2^0 - \frac{E_q}{6} \left[\frac{1}{E_n} \right]$$

$$\gamma_3 = \gamma_3^0 + \frac{E_q}{6} \left[\frac{1}{E_n} \right]$$

$$\kappa = \kappa^0 - \frac{1}{3} + \frac{E_q}{18} \left[\frac{7}{E_{\kappa}} - \frac{10}{E_n} \right]$$

$$q = \frac{2E_q}{9} \left[\frac{1}{E_{\kappa}} - \frac{1}{E_n} \right]$$

$$H_1 = -\frac{E_q}{3} \left[\frac{2}{E_{\kappa}} + \frac{1}{E_n} \right] \quad (\text{B4})$$

where $E_q = 2mQ^2/\hbar^2$. The expressions for κ and q are found by a comparison of terms when the magnetic field is included.

The Hamiltonian of equation (B2) can be converted to an effective-mass Hamiltonian for a magnetic field by adding the interaction of the spin with the magnetic field and by replacing k values with operators, which are written in terms of the creation and annihilation operators of a harmonic oscillator function.

$$\kappa_+ = \sqrt{\frac{2eH}{\hbar c}} a^+$$

$$k = \sqrt{\frac{2eH}{\hbar c}} a$$

$$\epsilon k^2 = \sqrt{\frac{\hbar e H}{mc}} \left(N + \frac{1}{2} \right), \quad (\text{B5})$$

where $N = a^+ a$. The effective-mass Hamiltonian operates on the 'modulating' functions which are shown, in part, along with their band-edge Bloch functions in equation (2). If we consider, for the moment, only the

lower 4×4 block in equation (B2), $\mathcal{H}_B$, a solution can be found with the functions of equation (2) if in the element (2, 3) $\gamma_+^0 k_-^2$ is retained but $\gamma_-^0 k_+^2$ is dropped. A similar situation holds for some of the terms in the $\Gamma_8^+ - \Gamma_6^-$ interaction and if, in effect, we set $\gamma_3 - \gamma_2$ equal to zero we can find a solution to the magnetic field problem. This is equivalent to the approximation made in Ref. [14]. Since we are now interested in the nonparabolicity which arises from the $\Gamma_8^+ - \Gamma_6^-$ interaction this approximation seems inappropriate. As an alternative we have replaced, in effect, $(\gamma_3 - \gamma_2)k_+^2$ by $(\gamma_1 - \gamma_2)k_-^2$, which again makes a solution of the magnetic field problem possible. The argument is that by ignoring a term proportional to k_+^2 we neglect a term of order n , but replacing k_+^2 by k_-^2 requires a correction of $(k_-^2 - k_+^2)$ which is of order 1. (Either approximation has the undesirable feature that correction terms, though small in net effect, are made up of opposite but nearly equal contributions from lower and higher levels.)

The elements being discussed are off-diagonal and of such a sign that the effect of neglecting $(\gamma_3 - \gamma_2)k_+^2$ is to overestimate the nonparabolic correction on the Γ_8^+ bands, and the effect of replacing this quantity by $(\gamma_1 - \gamma_2)k_-^2$ is to underestimate the correction. Although the second approximation should be better for the reasons mentioned above, there is still some uncertainty as to how well it actually works. To get more trustworthy results it is probably necessary to use the laborious, semiclassical approach of calculating cyclotron energies from the areas enclosed by constant energy contours. This cannot give the 'quantum effects' near $E(\Gamma_8^+)$ but should be superior to other methods at high n values because isotropic energy surfaces are not required.

A comparison between the approximate theories can be made on the classical (high n) values of the (100), Γ_8^+ cyclotron effective masses. These are found by reducing the larger dimension matrices to 2×2 , corresponding to the two Γ_8^+ bands. Analytical expressions for the energies are found by solving the corresponding secular determinant. In the high- n limit these give

$$(m/m^*)_{(100)} = -\gamma_1 \pm \sqrt{\gamma_2^2 l + (3/4)(\gamma_2 + \gamma_3)^2} \quad (\text{B6})$$

for the approximation of Ref [14], where the plus and minus sign correspond to the conduction and valence band masses, respectively. The approximation with $(\gamma_1 - \gamma_2)k_+^2$ replaced by $(\gamma_1 - \gamma_2)k_-^2$ leads to

$$(m/m^*)_{(100)} = -\gamma_1 \pm 2\gamma_2, \quad (\text{B7})$$

where the + sign now applies to the valence band. These are just the masses for the (100) directions, which are the 'lightest' directions in the (100) plane. The 'heaviest' directions in this plane are (110) for which

$$(m/m^*)_{(110)} = -\gamma_1 \pm \sqrt{\gamma_2^2 + 3\gamma_1^2}. \quad (\text{B8})$$

The masses in equation (B6) fall between those in equation (B7) and equation (B8) because $|\bar{\gamma}_2| < |\bar{\gamma}_3|$.

The exact, large n , (100) cyclotron masses for the 2×2 problem can be found from equation (A2); where the mass is determined from the derivative with respect to energy of the area enclosed by a constant energy contour. This procedure requires numerical integration and differentiation. However, if the square root in equation (A2) is expanded and truncated after the term $C^2 f / (2B^2)$, analytical expressions for the masses can be found, as shown in Ref. [8]. This gives

$$(m/m^*)_{(100)} = (-\bar{\gamma}_1 - 2\bar{\gamma}_2) \sqrt{1 - \bar{F}/8} \quad (\text{B9})$$

for the conduction band mass and a similar expression involving a valence band anisotropy parameter for the valence band mass.

The agreement between experiment and theory in Figs. 3 and 4 is nearly independent of which approximate theory is used as long as the masses predicted from that theory are those measured (Table I). However, the parameters which go into the theory do depend upon the particular approximation used. To minimize this effect, for the purpose of reporting a set of parameters for α -Sn, we have used equation (B9) for the conduction band mass since $\bar{F}$ has been experimentally determined, and have used a simple average of equations (B7) and (B8) for the valence band mass.

A final comment about the 7×7 and 4×4 Hamiltonians. The variation of conduction band g -factor as a function of energy from the band edge is much more rapid in the case of the 4×4 matrix than the 7×7 matrix. This suggests that it is important to take the variation of the Γ_{15} levels with magnetic field into account when calculating g -factors away from band edges for the Γ_8^+ , Γ_7^- and Γ_7^- bands.

THE PRESSURE AND TEMPERATURE DERIVATIVES OF THE ELASTIC CONSTANTS OF AgBr AND AgCl*

K. F. LOJE and D. E. SCHUELE

Case Western Reserve University, Cleveland, Ohio 44106, U.S.A.

(Received 9 July 1969; in revised form 21 November 1969)

Abstract—The ultrasonic pulse-echo method was used to measure the adiabatic elastic constants and their pressure and temperature derivatives for AgBr and AgCl at 300 and 195°K. The explicit temperature dependence of the elastic constants was calculated, and the value for the isothermal bulk modulus was found to be anomalously large. An ultrasonic equation of state was compared with Bridgman's compression data and the effect of the significantly nonlinear pressure dependence of the bulk modulus of AgBr was shown. High and low temperature limiting values of the Grüneisen parameter were calculated from the elastic data and compared with those calculated from available thermodynamic data.

1. INTRODUCTION

THE COHESIVE energy and lattice dynamics of the alkali halides have been the subject of numerous experimental and theoretical studies, all aimed at understanding the various interactions in these ionic crystals. Measurements of most of the elastic properties have already been completed and have been most useful, since, for example, the pressure derivatives of the elastic constants are particularly sensitive to the short range interionic repulsions and the temperature derivatives are helpful in assessing the anharmonicity in the lattice potential. Elastic measurements on the silver halides are a natural extension of this alkali halide work. AgF, AgCl and AgBr all have the NaCl structure (AgI has the zinc-blende structure), but they apparently are not purely ionic crystals. Interesting deviations from alkali halide-like behavior are thus expected and have been found. For example, the simple Born or Born-Mayer treatments of the cohesive energy, which have been so successful for the alkali halides, do not work so well for

the silver halides, as indicated in the review article by Tosi[1]. The Cauchy relation, $C_{12} = C_{11}$, holds reasonably well for most of the alkali halides, but it is violated significantly by AgBr and AgCl, indicating that noncentral forces play a major role in the binding. A shell model was applied by Joshi and Gupta[2] to AgCl, but the calculated phonon dispersion curves were in poor agreement with the experimental curves of Cole [3], whereas good results had been obtained using a shell model for NaI and KBr[4]. In short, the silver halides exhibit significant and interesting deviations from the alkali halides.

2. EXPERIMENTAL PROCEDURE

Sample preparation

Single crystals of AgBr and AgCl were purchased from the Harshaw Chemical Company in the form of right circular cylinders with diameter 0.75 in., length 1 in., and faces of approximately [110] orientation. All orientations were measured by a back reflection Laue X-ray technique, after liberally etching with a sodium thiosulfate (hypo) solution. Final acoustic surfaces were then prepared by polishing with No. 4/0 metallo-

*Work supported in part by the Atomic Energy commission.

graphic paper lubricated with kerosene and backed by plate glass. Such polishing produced sufficient surface distortion so that nearly polycrystalline Laue patterns resulted, but earlier polishing and etching tests showed that such surface distortion extended less than one mil in depth. The orientation of the AgBr sample was within 0.3° of the desired [110] direction. For the AgCl crystal, however, Laue photographs taken on opposite faces and at various points on the same face gave orientation variations as large as 1° . A similar problem with single crystal AgCl was noted by Arenberg[5]. The final polishing of the AgCl sample was done so that the center of one face was within 0.2° of the [110] direction.

A second single crystal of AgBr which will be denoted as AgBr II, was prepared from a large ingot also obtained from the Harshaw Chemical Company. It was ground in the form of a right circular cylinder of diameter 0.6 in., with the acoustic faces within 0.2° of the [110] direction.

Elastic constant measurements

A 10 mc/sec ultrasonic pulse-echo[6] technique was employed, the electronics set-up having been described in detail by Rotter[7] and by Wong and Schuele[8]. All zero pressure transit times were measured using the buffer technique[9]. Salol was used as the seal material at room temperature, Nonaq stopcock grease at dry ice temperature. The room temperature measurements were made with the transducer-buffer-crystal assembly mounted in a temperature-controlled enclosure set to regulate at 300°K . A thermocouple on the sample was used to measure its actual temperature. The 195°K transit times were measured with the transducer-buffer-sample assembly immersed in a dry ice-freon bath.

Pressure measurements

The general method of determining the pressure derivatives of the elastic constants

from the change in transit time with pressure has been described by Daniels and Smith[10]. The electronics is the same as that employed in the elastic constant measurements.

The relatively large transit time shifts encountered in AgBr and AgCl enabled all the $P=0$ pressure derivatives to be determined from runs restricted to 1 kbar maximum pressure. Pressure was determined by measuring the change in resistance of a 300 Ω coil of manganin wire, the coil always being kept at room temperature.

3. RESULTS

Table 1 lists the various physical and thermodynamic quantities used in the reduction of data. Since no experimental data were available for the thermal expansion of AgBr below room temperature, the 195°K value was obtained from the room temperature data using Grüneisen's law.

Elastic constants

Since AgCl and AgBr are cubic crystals, all three independent elastic stiffnesses can be determined from the velocities of the three pure sound waves which can be propagated along the [110] direction.

The results of the elastic constant measurements at 300 and 195°K are given in Table 2, along with values obtained from other investigators who also employed ultrasonic techniques. Examination of transit times measured with different buffer rods (in the case of shear waves) and at different times indicated that the transit times measured had a precision of better than 0.1%. The precisions of the various elastic constants are: AgBr- C'_{11} , 0.2%; C' , 0.3%; C_{11} , 0.3%; C_{12} , 0.3%; C_{12} , 0.5%; B_s , 0.4%; AgCl- C'_{11} , 0.2%; C' , 0.4%; C_{11} , 0.5%; C_{12} , 0.3%; C_{12} , 0.5%; B_s , 0.4%. The larger uncertainty in the directly measured shear modes, C' and C_{44} , in AgCl is due to the larger uncertainty in the orientation of the AgCl crystal, as mentioned above. The effect of this orientation uncertainty on the elastic constants

Table 1. Basic data used in this work for AgBr and AgCl. An Avogadro's number $6.02257 \times 10^{23} \text{ mole}^{-1}$ was used in computing the X-ray density, and a mechanical heat equivalent of 4.186 J cal^{-1} in computing the isothermal bulk modulus

	AgBr		AgCl	
	300°K	195°K	300°K	195°K
Sample length (cm)	2.2292	2.2214	2.2323	2.2255
Molecular weight	187.779	187.779	143.323	143.323
Lattice constant (Å)	5.7748 [11]	5.7546	5.5493 [12]	5.5324
X-ray density (g cm^{-3})	6.476	6.544	5.570	5.621
Linear thermal expansion coefficient, $\alpha (10^{-5} \text{ deg}^{-1})$	3.5 [13]	3.2†	3.1 [14]	2.7 [14]
$(d\alpha/dT)_p (10^{-8} \text{ deg}^{-2})$	2.8†	3.6†	3.6*	4.6*
Specific heat, $C_p (\text{cal mole}^{-1} \text{ deg}^{-1})$	12.5 [15]	12.2 [15]	12.8 [16]	11.8 [15]
$(dC_p/dT)_p^* (10^{-3} \text{ cal mole}^{-1} \text{ deg}^{-2})$	1.4	6.7	5.9	12.6
Isothermal bulk modulus, B_T ($10^{12} \text{ dyn cm}^{-2}$)	0.3770	0.4195	0.4174	0.4590

*Determined from corresponding α [14] and C_p [15–17].

†Obtained from Grüneisen's relation.

Table 2. Adiabatic elastic stiffnesses of AgBr and AgCl in units of $10^{12} \text{ dyn cm}^{-2}$

	C'_{11}	C'	C_{44}	C_{31}	C_{12}	B_s
AgBr (Room temp.)						
Author (300°K)	0.5164	0.1170	0.0724	0.5610	0.3270	0.4050
Tannhäuser, Bruner and Lawson [18], (26°C)			0.0720	0.563	0.328	0.406
Tannhäuser and Lawson [19], (28°C)			0.0728	0.562	0.328	0.406
AgBr (195°K)						
Author	0.5629	0.1450	0.0765	0.6313	0.3414	0.4381
AgCl (Room temp.)						
Author (300°K)	0.5423	0.1187	0.0624	0.5985	0.3611	0.4403
Hidshaw, Lewis and Briscoe [20], (300°K)			0.0616	0.5920	0.3640	0.4400
Arenberg [5]			0.0625	0.601	0.362	0.441
Vallin [21], (295°K)			0.0622	0.5860	0.3582	0.4341
AgCl (195°K)						
Author	0.5861	0.1427	0.0653	0.6635	0.3782	0.4733
Hidshaw, Lewis and Briscoe [20]			0.064	0.656	0.380	0.472
Vallin [21]			0.0650	0.6475	0.3730	0.4645

C'_{11} , C' and C_{44} are the directly measured quantities in the present work, and $C'_{11} = (C_{11} + C_{12} + 2C_{44})/2$, $C' = (C_{11} - C_{12})/2$ and $B_s = (C_{11} + 2C_{12})/3$.

was evaluated by carrying out the perturbation calculation of Neighbors[22] for a few of the different orientations determined from different Laue photographs of the AgCl crystal. No orientation corrections, however, have been incorporated in the values in Table 2.

The present results for AgBr are in excellent agreement with those of Tannhauser, Bruner and Lawson[18] and of Tannhauser and Lawson[19]. Larger variations are found, however, among the various results for AgCl, where all the values do not agree within their quoted experimental precisions. Comparison of the present results with the stiffnesses directly measured by Hidshaw, Lewis and Briscoe[20], namely C_{11} , C_{33} and C'_{11} , shows their values to be systematically lower. Vallin's[21] C_{11} value is lower than all others cited, causing his bulk modulus to be lower also.

Comparison of the elastic constants of AgBr and AgCl shows that AgBr, having the larger anion, is slightly more compressible but has a larger shear stiffness C'_{11} . The other shear stiffness, C' , is almost the same in both

materials. Thus AgCl has the larger elastic anisotropy, the ratio C'/C_{44} at room temperature being 1.90 for AgCl and 1.62 for AgBr. These anisotropies increase with decreasing temperature. Of particular note is the significant failure of the Cauchy condition, $C_{12} \approx C_{11}$. Here $C_{12} \approx 4.5 C_{44}$ for AgBr and $C_{12} \approx 5.8 C_{44}$ for AgCl, relationships that are nearly temperature independent.

Table 3 gives the isothermal elastic stiffnesses and the adiabatic and isothermal elastic compliances for AgCl and AgBr.

Temperature derivatives

The measured temperature derivatives of AgBr and AgCl at room temperature and dry ice temperature are listed in Table 4, along with the 300°K results of Hidshaw, Lewis and Briscoe[20] for AgCl and values for AgBr at 26°C obtained from graphical differentiation of the elastic constant data of Tannhauser, Bruner and Lawson[18]. The agreement for AgCl is good, while that for AgBr is adequate, in view of the uncertainties inherent in the graphical differentiation.

Table 3. Adiabatic and isothermal elastic stiffnesses, C , and adiabatic and isothermal elastic compliances, S , for AgBr and AgCl

	C_{11}	C_{12}	C_{33}	S_{11}	S_{12}	S_{33}
AgBr (300 K)						
adiabatic	0.5610	0.3270	0.0724	3.123	1.150	13.81
isothermal	0.5330	0.2990	0.0724	3.144	1.130	13.81
AgBr (195 K)						
adiabatic	0.6313	0.3414	0.0765	2.553	-0.896	13.07
isothermal	0.6128	0.3229	0.0765	2.564	0.885	13.07
AgCl (300 K)						
adiabatic	0.5985	0.3611	0.0624	3.061	1.152	16.01
isothermal	0.5756	0.3382	0.0624	3.075	1.138	16.01
AgCl (195 K)						
adiabatic	0.6635	0.3782	0.0653	2.571	0.933	15.32
isothermal	0.6492	0.3638	0.0653	2.578	0.925	15.32

Units are 10^{11} dyn cm $^{-2}$ for C and 10^{-12} cm ^{2} dyn $^{-1}$ for S

Table 4. Temperature derivatives of the adiabatic elastic stiffnesses of AgBr and AgCl. Units are 10^{-4} deg^{-1}

	C'_{11}	C'	$(d \ln C/dT)_p$		C_{12}	B_s
	C_{44}	C_{33}				
AgBr (Room Temp.)						
Author (300°K)	- 8.62	-22.0	-5.48	-11.82	-4.54	7.90
Tannhauser, Bruner and Lawson* (26°C)			-5.5	-9.5	-4.0	
AgBr (195°K)						
Author	- 7.49	-19.1	-4.88	-10.47	-3.16	-6.67
AgCl (Room Temp.)						
Author (300°K)	-7.84	-18.8	-4.15	-10.40	-4.89	-7.38
Hidshaw, Lewis and Briscoe [20], (300°K)			-4.21	-10.48	-4.95	
AgCl (195°K)						
Author	- 7.15	-16.9	-4.26	-9.53	-3.97	-6.57

* Values determined from graphical differentiation of data of Ref. [18].

An overall examination of Table 4 reveals that AgBr and AgCl are very similar, with AgCl undergoing smaller percentage changes between 300 and 195°K. Thermodynamics predicts that $d \ln C/dT$ vanishes at absolute zero, so a decrease in the magnitude of the temperature derivative is expected as the temperature is lowered. The only anomaly occurs for C_{44} in AgCl, where the measured 195°K temperature derivative is 1.4 per cent larger in magnitude than the 300°K value. This anomaly was carefully verified as each of these listed values is an average obtained from three experimental runs, including a differential experiment in which the room temperature and dry ice temperature derivatives were measured consecutively using the same echo number and the same Nonaq crystal-transducer seal.

The multiple runs made on C_{44} in AgCl provide a basis for estimation of the precision of the temperature derivative measurements. For both AgBr and AgCl, the precisions of the $d \ln C/dT$ for the directly measured C'_{11} , C' , and C_{44} are estimated to be 1 per cent,

while for the other modes: C_{11} , 1%; C_{12} , 4%; B_s , 2%.

Pressure results

For a pressure run the measured change in transit time of the n th echo, Δt_n , was obtained as a function of the change in pressure gauge resistance, ΔR_g . Typical data plots are shown in Fig. 1. At room temperature there was a small but noticeable nonlinearity for all measured modes in both AgBr and AgCl, the nonlinear contribution to Δt_n at 1 kbar being the order of 2 per cent. At 195°K the nonlinearities were smaller, nearly undetectable in plots like those of Fig. 1. For each run the initial slope of the Δt_n vs. ΔR_g curve was obtained by fitting the experimental data to a second degree polynomial using the method of least squares. For the nearly-linear 195°K data, the resulting initial slopes were in excellent agreement with those determined by fitting straight lines to the lower data points (below 0.5 kbar), thus giving credibility to the least squares quadratic curve fitting. The initial slope, combined with

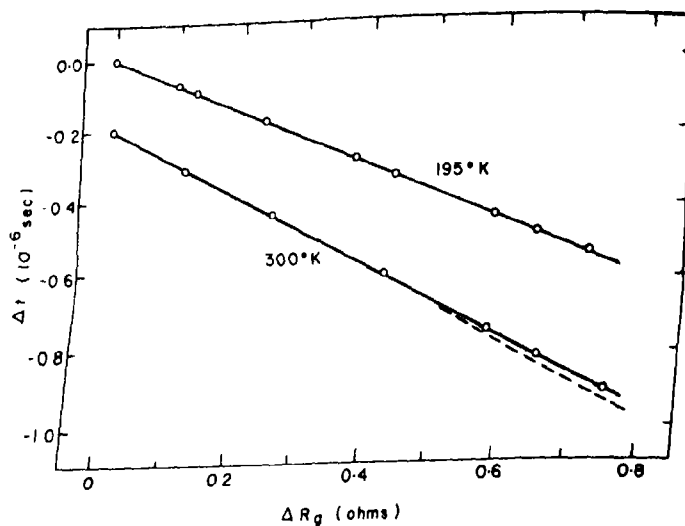


Fig. 1. Typical data plots showing the shift in arrival time vs. change in pressure gauge resistance for the 6th echo of the longitudinal wave propagating in the [110] direction in AgBr. The zero pressure transit times per echo are 15.788 μ sec at 300°K and 15.148 μ sec at 195°K. The pressure gauge constant is 1.409 kbar/ Ω . The dashed line is the linear extension of the low pressure points. The two curves are displaced for the sake of clarity.

the pressure gauge constant and appropriate n th echo transit time at zero pressure, taken from the previous elastic constant measurements, gave the quantity $d \ln t / dP$, the fractional transit time shift with pressure. The pressure derivative of the corresponding elastic constant was then calculated from

$$\frac{d \ln C}{dP} = \frac{1}{3B_T} - 2 \frac{d \ln t}{dP} \quad (1)$$

where B_T is the isothermal bulk modulus.

The results of the pressure measurements on AgBr and AgCl are presented in Tables 5 and 6 in several forms. The logarithmic derivative $d \ln C / d \ln r$, where r is a crystal distance, was calculated from $d \ln C / d \ln r = -3B_T d \ln C / dP$. No systematic differences were found between the runs made with salol seals and those with Nonaq seals, or among runs made on different echoes of the same wave. The number of runs averaged to give the final results are also included in the tables. For both AgBr and AgCl, the pre-

cisions of the dC/dP for the directly measured C'_{11} , C' , and C_{11} are set at 2 per cent, while for other stiffnesses: C_{11} , 2%; C_{12} , 5%; B_s , 3%.

Examination of Tables 5 and 6 reveals that AgBr and AgCl are very similar in their behavior under pressure, with AgCl generally exhibiting smaller percentage changes between 300 and 195°K, as was the case for the measured temperature derivatives. It may be noted that the derivatives dC/dP and $d \ln C / d \ln r$ are less temperature dependent than $d \ln C / dP$. All the $d \ln C / dP$ decrease algebraically as the temperature decreases, however, a comparison of this kind in terms of the dC/dP 's shows the shear constant C' to be anomalous in that its derivative at 300°K is slightly smaller than that at 195°K, although the values are actually in agreement within experimental error.

The shear stiffness C_{41} is of particular interest in that it exhibits a very small pressure dependence, just as it had a small temperature dependence. It also possesses the unusual property of a negative pressure

Table 5. Results of pressure measurements for AgBr expressed in several forms

		No. of Runs	$d \ln t/dP$	$d \ln C/dP$	$d \ln C/d \ln r$	dC/dP
C'_{11}	300°K	6	-7.27	15.4	-17.5	7.97
	195°K	2	-5.95	12.7	-16.0	7.15
C'	300°K	4	-15.07	31.0	-35.1	3.63
	195°K	2	-12.19	25.2	-31.7	3.65
C_{44}	300°K	5	2.24	-3.60	4.07	-0.261
	195°K	1	2.54	-4.28	5.39	-0.328
C_{11}	300°K			21.1	-23.9	11.9
	195°K			17.6	-22.2	11.1
C_{12}	300°K			14.1	-15.9	4.60
	195°K			11.2	-14.1	3.83
B_s	300°K			17.3	-19.6	7.02
	195°K			14.3	-18.0	6.26

t is the acoustic wave transit time in the crystal and r is a crystal distance. Units of $d \ln t/dP$ and $d \ln C/dP$ are $10^{-12} \text{ dyn}^{-1} \text{ cm}^2$.

Table 6. Results of pressure measurements for AgCl expressed in several forms

		No. of Runs	$d \ln t/dP$	$d \ln C/dP$	$d \ln C/d \ln r$	dC/dP
C'_{11}	300°K	4	-6.19	13.2	-16.5	7.15
	195°K	2	-5.36	11.4	-15.8	6.70
C'	300°K	7	-13.4	27.6	-34.6	3.28
	195°K	3	-11.3	23.3	-32.1	3.33
C_{11}	300°K	4	4.46	-8.12	10.2	0.507
	195°K	2	4.59	-8.46	11.6	-0.552
C_{11}	300°K			18.3	-22.9	10.9
	195°K			15.9	-22.0	10.6
C_{12}	300°K			12.1	-15.2	4.38
	195°K			10.4	-14.3	3.93
B_s	300°K			14.9	-18.7	6.57
	195°K			13.0	-17.9	6.15

t is the acoustic wave transit time in the crystal and r is a crystal distance. Units of $d \ln t/dP$ and $d \ln C/dP$ are $10^{-12} \text{ dyn}^{-1} \text{ cm}^2$.

derivative, the acoustic transit time actually increasing and C_{44} decreasing as pressure is applied.

Pressure results—10 kilobars

In the pressure work to 10 kbar on the AgBr II crystal, two runs, each on a different echo number, were made for each of the three measured modes, C'_{11} , C' , and C_{44} . A typical example of the curvature in the Δt_n vs. ΔR_q data is given by the plot of a C' run in Fig. 2, in which a linear term has been subtracted

from the data. For each measured mode, the nonlinear contributions to Δt_n at 10 kbar were the order of 20 per cent. The zero pressure transit times needed in the reduction of the pressure data were measured using the buffer technique, the adiabatic elastic constants computed from them indicating this crystal to be slightly stiffer than the AgBr crystal used in the 1 kbar work, the values of C'_{11} , C' and C_{44} being larger by 0.2, 0.1 and 0.5 per cent, respectively, than those in Table 2.

To compute the bulk modulus as a function

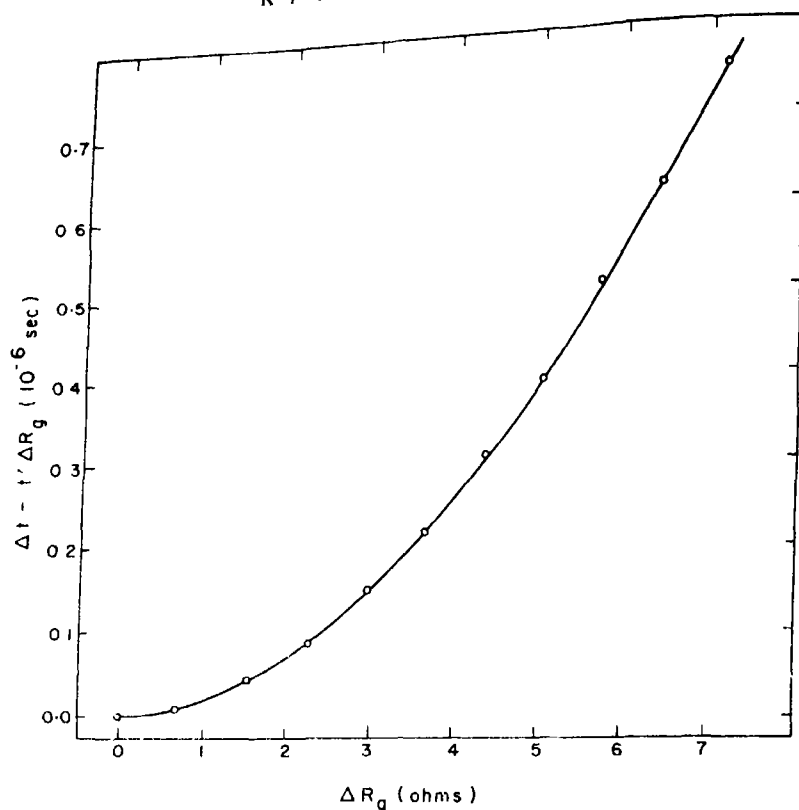


Fig. 1. Illustration of the nonlinearity in the 10 kbar pressure data. The above data is for the C' shear wave propagating in the [110] direction in AgBr. Δt is the shift in arrival time of the 1st echo, ΔR_g the change in pressure gauge resistance, and t' the zero pressure slope determined from a least squares third order fit of the data. The pressure gauge constant is 1.003 kbar/ Ω . The zero pressure transit time is 24.842 μ sec, and $t' = 0.5138 \mu$ sec/ Ω .

of pressure for use in an equation of state analysis, an analytic expression for the transit time of each measured acoustic mode as a function of pressure was needed. For a particular mode the transit time, $t(P)$, can be represented by a series expansion in powers of the pressure, P , as

$$t(P) = t_0 + t'_0 P + \frac{1}{2} t''_0 P^2 + \frac{1}{6} t'''_0 P^3 \quad (2)$$

where the primes denote differentiation with respect to pressure and the coefficients are all evaluated at zero pressure. Here t_0 is the zero pressure transit time, $[t(P) - t_0]$ is the transit

time shift, Δt_n , directly measured in a pressure run, and t'_0/t_0 is just $d \ln t/dP$, a quantity also determined in the 1 kbar pressure runs. The coefficients t'_0 , t''_0 , and t'''_0 were all evaluated from the 10 kbar data by two different procedures: (1) fitting a third order polynomial to the Δt_n vs. ΔR_g data using the method of least squares, and (2) employing a method of successive approximations. The results from the two procedures were in satisfactory agreement, however, more confidence was had in the latter procedure, since the effects of higher order terms are graphically displayed.

The final results from the method of successive approximations are most usefully expressed in terms of the dimensionless quantity $\Delta t/t_0$, which is independent of both crystal length and echo number, and are:

$$\begin{aligned} C'_{11}: \frac{\Delta t}{t_0} &= [-7.20 P + 0.145 P^2 \\ &\quad - 0.0027 P^3] \times 10^{-3} \\ C': \frac{\Delta t}{t_0} &= [-14.77 P + 0.383 P^2 \\ &\quad - 0.0079 P^3] \times 10^{-3} \\ C_{44}: \frac{\Delta t}{t_0} &= [2.27 P + 0.041 P^2 \\ &\quad - 0.0004 P^3] \times 10^{-3} \end{aligned} \quad (3)$$

where P is in kilobars. The linear coefficient for each mode is approximately 1 per cent larger (algebraically) than the corresponding $d \ln t/dP$ value obtained from the 1 kbar work on AgBr, as reported in Table 5.

4. INTERPRETATION

Temperature dependence of the elastic constants

A quantity of theoretical interest is the explicit temperature dependence of an elastic

constant, which can be evaluated by combining the present pressure and temperature data. Specifically,

$$\left(\frac{d \ln C}{dT} \right)_P = \left(\frac{d \ln C}{dT} \right)_V + \alpha \left(\frac{d \ln C}{d \ln r} \right)_T \quad (4)$$

The first term is the measured constant pressure temperature coefficient, the second term represents the desired explicit temperature dependence, and the third term represents the dependence on the volume dilatation accompanying a temperature change. The individual terms in this equation are given in Tables 7 and 8 for AgBr and AgCl.

The explicit temperature dependence of the shear constants C' and C_{44} is much larger (in magnitude) than it is in the alkali halides LiF, NaF, NaCl and KCl [23, 24], the fluorites CaF₂ and BaF₂ [25], or the noble metals [26]. Comparably large values have been found, however, in Pb [27]. The values of $(d \ln B_S/dT)_V$ and $(d \ln B_T)_V$ for both AgBr and AgCl are of particular interest. Swenson [28] has analyzed room temperature data for a variety of cubic materials and found that $(d \ln B_S/dT)_V$ is ordinarily positive and that $(d \ln B_T/dT)_V$ is small, almost always of magnitude less than 10^{-4} deg^{-1} . The deviations of AgBr and AgCl from these general

Table 7. Constitution of the temperature derivatives of the elastic constants of AgBr. Units are 10^{-4} deg^{-1}

$(d \ln C/dT)_P = (d \ln C/dT)_V + \alpha(d \ln C/d \ln r)_T$			
C'_{11}	300°K	-8.62	-2.51
	195°K	-7.49	-2.37
C'	300°K	-22.0	-9.7
	195°K	-19.1	-9.0
C_{44}	300°K	-5.48	-6.91
	195°K	-4.88	-6.60
C_{11}	300°K	-11.82	-3.45
	195°K	-10.47	-3.37
C_{12}	300°K	-4.54	1.03
	195°K	-3.16	1.36
B_s	300°K	-7.90	-1.04
	195°K	-6.67	-0.91
B_T	300°K	-10.8	-2.9
	195°K	-9.3	-3.1

Table 8. Constitution of the temperature derivatives of the elastic constants of AgCl. Units are 10^{-4} deg^{-1}

$(d \ln C/dT)_P = (d \ln C/dT)_V + \alpha(d \ln C/d \ln r)_T$			
C_{11}	300°K	-7.84	-2.72
	195°K	7.15	-2.90
C'	300°K	-18.8	-8.1
	195°K	-16.9	-8.2
C_{11}	300°K	4.15	-7.30
	195°K	-4.26	-7.40
C_{12}	300°K	10.40	-3.31
	195°K	-9.53	-3.61
C_{12}	300°K	4.89	-0.18
	195°K	-3.97	-0.11
B_0	300°K	7.38	-1.59
	195°K	6.57	-1.74
B_1	300°K	9.7	-3.2
	195°K	8.6	-3.4

results are significant, although the differences between corresponding $(d \ln B_0/dT)_P$ and $(d \ln B_0/dT)_V$ are quite normal. One practical result of this anomaly is that the simple relations between adiabatic and isothermal elastic data, which Swenson derived on the assumption that B_T was explicitly temperature independent, are not very good here.

Equation of state

Anderson[29] has recently shown how ultrasonic measurements at low pressures can successfully be used to predict the compression of solids at high pressures with the Murnaghan logarithmic equation of state,

$$\ln \left(\frac{V}{V_0} \right) = \frac{1}{B_0'} \ln \left[\frac{B_0'}{B_0} P + 1 \right] \quad (5)$$

where V_0 , B_0 and B_0' are, respectively, the zero pressure volume, isothermal bulk modulus and its pressure derivative. Anderson applied the Murnaghan equation to a variety of materials for which ultrasonic data are available, covering several structure types and a wide range of compressibilities, and compared the predicted compression with available experimental results at high pressures.

The present 1 kbar ultrasonic data was used to compute B_0 and B_0' for both AgBr and AgCl at room temperature, the resulting plots of the Murnaghan equation being given in Figs. 3 and 4. The values used are: AgBr— $B_0 = 377.0$ kbar, $B_0' = 7.53$; AgCl— $B_0 = 417.4$ kbar, $B_0' = 7.00$.

Figures 3 and 4 also include the experimental compressions of Bridgman, both his measurements to 50 kbar[30] and his later work to 100 kbar[31]. An unidentified transition, easily seen in the figures, was found in AgBr at 86 kbar and a similar one in AgCl at 90 kbar. There is good agreement of the 50 kbar results with the Murnaghan curves, especially for AgCl, but in both cases the 100 kbar results show a significant deviation from the curve, the experimental values indicating the materials to be much more compressible at higher pressures than predicted by the Murnaghan equation.

The only assumption involved in deriving the Murnaghan equation is that the isothermal bulk modulus is a linear function of pressure, thus the failure of the equation for AgBr and AgCl must be due to higher order terms in the bulk modulus being significant in the relatively low pressure range covered by Bridgman's data. If the expansion of the bulk modulus is carried out to second

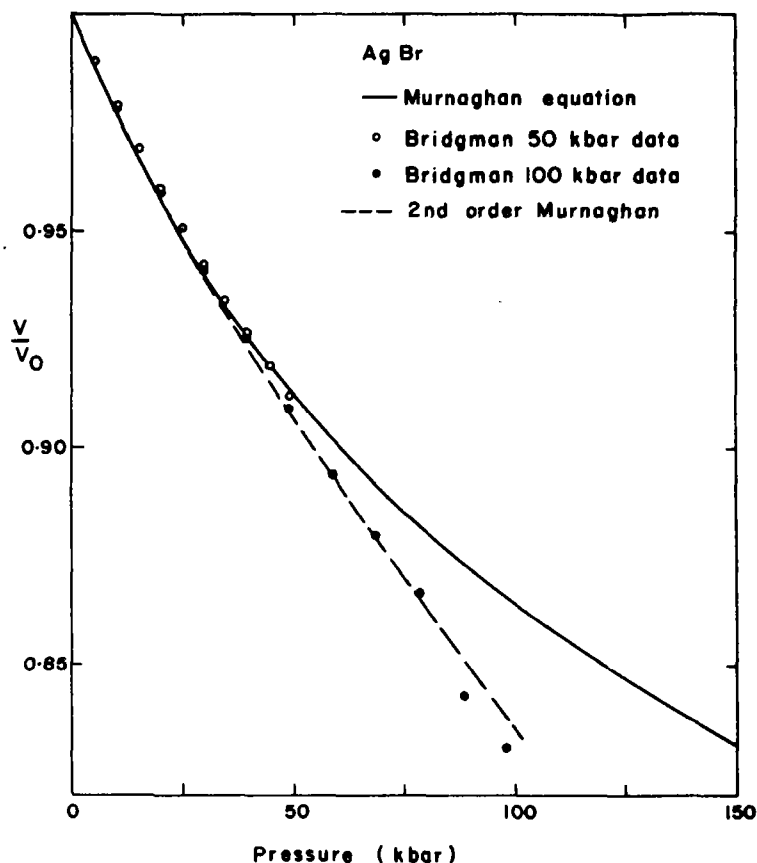


Fig. 3. The compression of AgBr at room temperature from Bridgman and as predicted from the ultrasonic data.

order, that is, if it is assumed that

$$-\left(\frac{\partial P}{\partial \ln V}\right)_T = B_T(P) = B_0 + B'_0 P + \frac{1}{2} B''_0 P^2 \quad (6)$$

then integration yields a 'second order Murnaghan equation':

$$\ln\left(\frac{V}{V_0}\right) = \frac{1}{A} \ln \left[\frac{B''_0 P / (B'_0 + A) + 1}{B''_0 P / (B'_0 - A) + 1} \right] \quad (7)$$

where $A^2 = (B'_0)^2 - 2B_0 B''_0$.

This equation was used to compute the compression of AgBr at room temperature with B_0 , B'_0 , and B''_0 values obtained from the 10 kbar data on the AgBr 2 crystal. B_0 and B'_0

were calculated from the measured B_S and dB_S/dP using the exact thermodynamic relations, the resulting values being in excellent agreement with those from the 1 kbar measurements; thus the Murnaghan curves for the two AgBr crystals measured are indistinguishable. The second derivative of the adiabatic bulk modulus at $P = 0$, B''_S , was then calculated from the ultrasonic data using an exact equation from Rotter[7]:

$$B''_S = -2 \sum_i C_i \left[\left(\frac{t'_0}{t_0} \right) - 3 \left(\frac{t'_0}{t_0} \right)^2 \right] + \frac{6B_0(dB_S/dP) - 3B_S B'_0 - B_S}{9(B_0)^2} \quad (8)$$

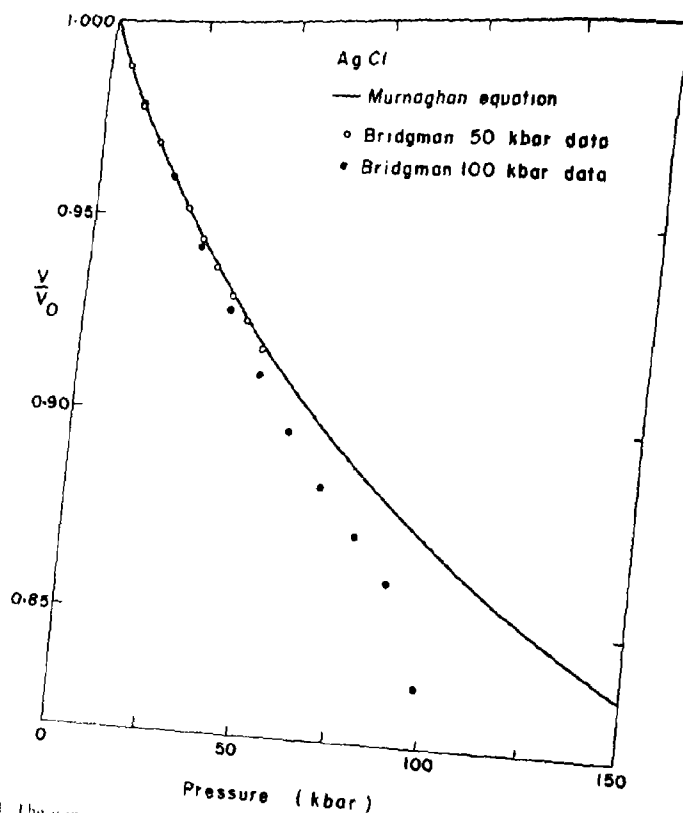


Fig. 4. The compression of AgCl at room temperature from Bridgman and as predicted from the ultrasonic data.

where the summation is over the three measured modes and is taken in the same sense as

$$B_T = \sum_i C_i = C'_0 + C'_{11} + \frac{1}{3}C''.$$

The quantities (t'_0/t_0) and (t''_0/t_0) are the coefficients of the linear and quadratic terms, respectively, in equation (3). Because of the lack of much of the needed thermodynamic data, no adiabatic-isothermal correction was employed in obtaining B''_0 , rather it was assumed that $B''_0 = B'_0$. Since the calculated compression is relatively insensitive to B''_0 , this assumption is well-founded as well as con-

venient. The resulting expression for the bulk modulus of AgBr is

$$B_T(P) = 377.7 + 7.49P - \frac{1}{2}(0.0287)P^2 \quad (9)$$

where B_T and P are in kilobars; the 'second order Murnaghan equation' obtained using this expression is shown as a broken curve in Fig. 3. Two features are of note: (1) the inclusion of the second order term in B_T significantly affects V/V_0 at pressures even below 100 kbar, and (2) the agreement with the experimental data of Bridgman below the transition pressure is excellent.

Anderson's conclusion that ultrasonic data

can be used to predict compressions at pressures one or two orders of magnitude larger than those employed in the ultrasonic measurements is still valid for AgBr and AgCl if interpreted properly. Since the ultrasonic data alone yield a significant nonlinear term in the bulk modulus, this term should therefore be included in computing the equation of state, in preference to using the ordinary Murnaghan equation.

Grüneisen parameter

The anharmonic character of the crystal potential energy, which results in thermal expansion, is related to the volume dependence of the normal mode frequencies of the lattice within the framework of the quasi-harmonic approximation. This dependence is usually discussed in terms of the dimensionless quantity called a mode gamma, γ_i , associated with a particular normal mode frequency, ω_i , where

$$\gamma_i \equiv -\frac{d \ln \omega_i}{d \ln V} \quad (10)$$

in which V is the crystal volume.

Table 9 gives the calculated low frequency mode gammas [10] of AgBr and AgCl for the longitudinal and transverse acoustic branches in the three principal crystal symmetry direc-

tions. Except for $\gamma(C_{44})$, the results for AgBr and AgCl are very similar, with the γ 's for the two materials nearly the same at 195°K. The C_{44} modes have negative gammas, with those in AgCl being almost twice as negative.

Using the Quasi-harmonic approximation, the macroscopic Grüneisen parameter, γ_G , as defined by

$$\gamma_G = \frac{3\alpha VB_s}{C_p} \quad (11)$$

can be shown to be a weighted average of the individual mode gammas. In particular, for a crystal of N atoms,

$$\gamma_G = \frac{\sum \gamma_i c_i}{\sum c_i} \quad (12)$$

where the summations are over the $3N$ normal modes and the weighting factor, c_i , for a given mode is the Einstein heat capacity of that mode. The variation of γ_G with temperature is thus due to the temperature dependence of the c_i and the implicit temperature dependence of the γ_i .

In the limit of high temperatures, all the normal modes are excited and all the c_i are equal, so γ_G becomes a simple average of the $3N$ values of γ_i . An estimate of this high temperature limiting value, $\bar{\gamma}_H$, can be

Table 9. Low frequency acoustic mode gammas for the three principal crystal directions and the high and low temperature Grüneisen parameters for AgBr and AgCl, obtained from elastic data

Gamma	Mode	AgBr		AgCl	
		300°K	195°K	300°K	195°K
$\gamma(C'_{11})$	[110] long.	2.74	2.50	2.59	2.46
$\gamma(C')$	[110] Trans.	5.68	5.12	5.60	5.18
$\gamma(C_{44})$	[110] Trans.	-0.85	-1.06	-1.86	-2.11
$\gamma(C_{11})$	[100] Long.	3.82	3.53	3.65	3.49
$\gamma(C_{44})$	[100] Trans.	-0.85	-1.06	-1.86	-2.11
$\gamma(C_l)$	[111] Long	2.34	2.09	2.18	2.05
$\gamma(C_t)$	[111] Trans.	4.14	3.82	4.04	3.83
γ_H	(high T limit)	2.39	2.13	2.03	1.85
γ_L	(low T limit)	1.63	1.24	0.93	0.58

obtained from the present elastic data if several assumptions are made; as described by Schuele and Smith[32]. This averaging was carried out using a computer program which effectively samples nearly 10^4 directions in the zone. The results of the calculations for AgBr and AgCl are listed in Table 9. Since the mode gammas all increase with increasing temperature, the $\bar{\gamma}_H$ computed from the elastic data at 300°K is larger than that computed from the data at 195°K.

At very low temperatures, only the low frequency, nondispersive acoustic modes are excited, so the crystal behaves as an elastic continuum and Debye theory holds. For a given branch of the acoustic spectrum, all excited modes have the same γ_i and the number of such modes is proportional to $C_i^{3/2}$, where C_i is the effective elastic stiffness for that branch. Thus the weighting factor for a particular γ_i in equation (12) is just the corresponding $C_i^{3/2}$. The computation of this

low temperature value of Grüneisen's gamma, γ_L , was carried out as part of the same computer program used to obtain $\bar{\gamma}_H$. Values were again calculated from both the 300°K elastic data and the 195°K data, with the results listed in Table 9.

The $\bar{\gamma}_L$ value from the 300°K data is larger than that from the 195°K data because of the larger γ_i at 300°K. Why $\bar{\gamma}_L$ is lower than $\bar{\gamma}_H$ can be understood by reference to Figs. 5 and 6, which are plots of the three acoustic mode gammas and effective elastic stiffnesses around the periphery of the triangle bounded by [100], [110] and [111]. These plots are for AgCl at room temperature; corresponding ones for AgCl at 195°K and for AgBr are very similar. $\bar{\gamma}_H$ is an unweighted average of the mode gammas, whereas in the calculation of $\bar{\gamma}_L$, modes with a low stiffness get heavily weighted. Thus the shear-type modes (subscripts 1 and 2 in the figures) have heavier weighting than the longitudinal-type modes

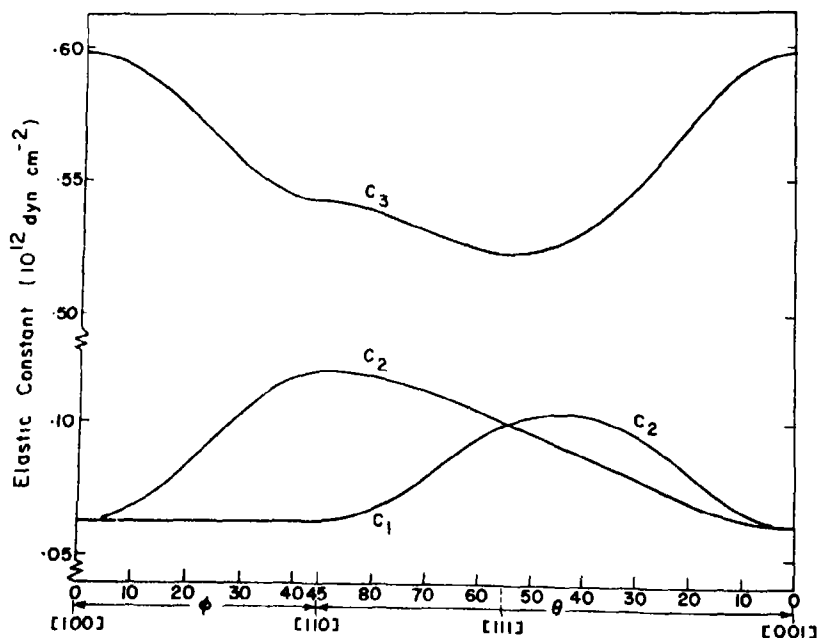


Fig. 5. Illustration of the elastic anisotropy of AgCl at room temperature. C_1 , C_2 , and C_3 are the ρv^2 for the slow shear, fast shear and longitudinal waves, respectively. Note the breaks in the ordinate axis.

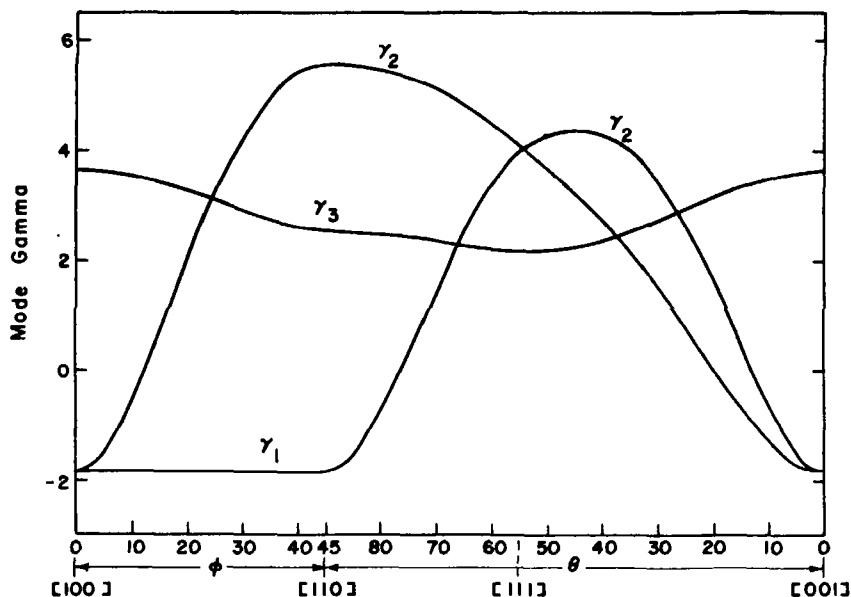


Fig. 6. Illustration of the anisotropy of the mode gammas for the three acoustic modes in AgCl at room temperature. γ_1 , γ_2 and γ_3 are for the slow shear, fast shear, and longitudinal waves, respectively.

(subscript 3), and of even more significance is that the lower shear γ_i 's are more heavily weighted than the higher shear γ_i 's. Consequently, $\bar{\gamma}_L$ is smaller than $\bar{\gamma}_H$, and the difference between the two values is greater in AgCl because of its more negative γ_i values.

A plot of the thermodynamic Grüneisen parameter for AgCl, obtained from equation (11), is shown in Fig. 7. Values of C_p were taken from Kobayashi[16], who smoothly couples his data above room temperature with that of Eastman and Milner[15] below room temperature. B_s and V were from Hidshaw, Lewis, and Briscoe[20]. Two sets of data for α were employed, one from Nicklow and Young[14] and one from Sreedar[33]. The γ_G values computed using Nicklow and Young's data show only a small change with temperature, while those calculated using Sreedar's data exhibit a significant temperature dependence. White[34] gives plots of the thermodynamic Grüneisen parameter to low

temperatures for a number of the alkali halides. One general result is that a drop in γ_G at low temperatures, if it occurs at all, occurs mainly between $\theta_D/10$ and $\theta_D/5$, where θ_D is the Debye temperature. For AgCl, θ_D calculated from the 0°K elastic constants is $\sim 160^\circ\text{K}$ [20]. Reasonably assuming that the variation of γ_G with temperature for AgCl should be similar to that in the alkali halides, a large drop in γ_G above 100°K, as results from Sreedar's data, is not expected. Thus the conclusion of Nicklow and Young that Sreedar's values are too low is given further support here.

Following Bartels and Schuele[24], an estimate of the low temperature limit of γ_G can be obtained by assuming that a value of $\bar{\gamma}_L$ calculated from elastic data at a particular temperature is proportional to the volume of the crystal at that temperature, and on this basis performing a linear volume extrapolation to 0°K of the 300 and 195°K values of $\bar{\gamma}_L$. The needed molar volumes at 0°K, 195 and 300°K were taken from Vallin[21]. The

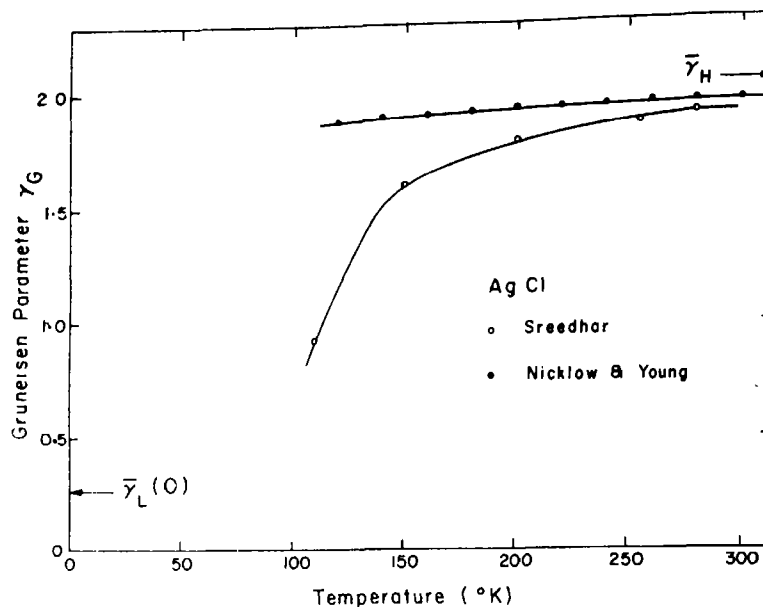


Fig. 7 The thermodynamic Gruneisen parameter of AgCl as a function of temperature, and its high and low temperature limiting values as calculated from the elastic data

0°K extrapolated value, denoted by $\bar{\gamma}_L(0)$, is 0.25 for AgCl and is shown in Fig. 7. Measurements of the thermal expansion of AgCl at low temperatures, particularly down to the 'T' region, would be most welcome as they would permit a comparison of γ_G with $\bar{\gamma}_L(0)$.

The thermodynamic value of γ_G at 300°K is in good agreement with the γ_H computed from the 300°K elastic data. Such agreement has not been the case for all materials for which a similar comparison has been made [25, 32], so the agreement may be fortuitous and not necessarily validate the assumptions involved in interpreting the elastic $\bar{\gamma}_H$ as the high temperature limit of the thermodynamic γ_G .

A plot of the thermodynamic Gruneisen parameter as a function of temperature for AgBr cannot be made because of the lack of thermal expansion data below room temperature, but the values of $\bar{\gamma}_H$ and $\bar{\gamma}_L$ computed from the present elastic data clearly predict

a decrease in γ_G at low temperatures, with the magnitude of the decrease being less than in AgCl. The room temperature value of γ_G , as computed from the data in Table 1, is 2.36, in excellent agreement with the 2.38 value of $\bar{\gamma}_H$ at 300°K.

REFERENCES

1. TOSI M. P., *Solid State Physics* (Edited by F. Seitz and D. Turnbull), Vol. 16, p. 1. Academic Press, New York (1966).
2. IOSHI S. K. and GUPTA R., *Phys. Rev.* **126**, 933 (1962).
3. COLE H., *J. appl. Phys.* **24**, 482 (1953).
4. COWLEY R. A., COCHRAN W., BROCKHOUSE B. N. and WOODS A. D. B., *Phys. Rev.* **131**, 1030 (1963).
5. ARENBERG D. I., *J. appl. Phys.* **21**, 941 (1950).
6. HUNTINGTON H. B., *Phys. Rev.* **72**, 321 (1947).
7. ROTTER C., Case Institute of Technology, Ph.D. Thesis (1966).
8. WONG C. and SCHUELE D. E., *J. Phys. Chem. Solids* **28**, 1225 (1967).
9. McSKIMIN H. J., *J. acoust. Soc. Am.* **33**, 606 (1961).
10. DANIELS W. B. and SMITH C. S., *The Physics and Chemistry of High Pressure*, p. 50. Society of Chemical Industry, London (1963).
11. *National Bureau of Standards Circ.* 539 **4**, 46 (1953).
12. *National Bureau of Standards Circ.* 539 **4**, 44 (1953).

13. STRELKOW P. G., *Phys. Z. Sowj.* **12**, 77 (1937).
14. NICKLOW R. M. and YOUNG R. A., *Phys. Rev.* **129**, 1936 (1963).
15. EASTMAN E. D. and MILNER R. T., *J. chem. Phys.* **1**, 444 (1933).
16. KOBAYASHI K., *Sci. Rep. Inst. Tohoku Univ.* **34**, 112 (1950).
17. KANZAKI H., *Phys. Rev.* **81**, 884 (1951).
18. TANNHAUSER D. S., BRUNER L. J. and LAWSON A. W., *Phys. Rev.* **102**, 1276 (1956).
19. TANNHAUSER D. S. and LAWSON A. W., *J. Chem. Phys.* **22**, 2092 (1954).
20. HIDSHAW W., LEWIS J. T. and BRISCOE C. V., *Phys. Rev.* **163**, 876 (1967).
21. VALLIN J., *Ark. Fys.* **34**, 367 (1967).
22. NEIGHBORS J. R., *J. acoust. Soc. Am.* **26**, 865 (1954).
23. MILLER R. A. and SMITH C. S., *J. Phys. Chem. Solids* **25**, 1279 (1964).
24. BARTELS R. A. and SCHUELE D. E., *J. Phys. Chem Solids* **26**, 537 (1964).
25. WONG C. and SCHUELE D. E., *J. Phys. Chem. Solids* **29**, 1309 (1968).
26. NEIGHBORS J. R. and ALERS G. A., *Phys. Rev.* **111**, 707 (1958).
27. MILLER R. A. and SCHUELE D. E., *J. Phys. Chem. Solids* **30**, 589 (1969); also USAEC Report No. 51, Contract AT(11-1)-623 (1968).
28. SWENSON C. A., *J. Phys. Chem Solids* **29**, 1337 (1968).
29. ANDERSON O. L., *J. Phys. Chem. Solids* **27**, 547 (1966).
30. BRIDGMAN P. W., *Proc. Am. Acad. Arts Sci* **74**, 21 (1940).
31. BRIDGMAN P. W., *Proc. Am. Acad. Arts Sci.* **76**, 1 (1945).
32. SCHUELE D. E. and SMITH C. S., *J. Phys. Chem Solids* **25**, 801 (1964).
33. SREEDHAR A. K., *J. Ind. Inst. Sci.* **A36**, 186 (1954).
34. WHITE G. K., *Proc. R. Soc.* **A286**, 204 (1965).

CURRENT CONTROLLED NEGATIVE RESISTANCE IN SEMICONDUCTORS

RICHARD S. CRANDALL

RCA Laboratories, Princeton, N. J. 08540, U.S.A.

(Received 30 June 1969; in revised form 14 November 1969)

Abstract—A model is proposed for the current controlled negative resistance observed in compensated semiconductors. An increase in the free carrier density due to impact ionization causes an increase in the free electron screening of the electron-phonon and electron-impurity interactions. The resulting decrease in electron scattering causes a heating of the electron gas and more impact ionization. This positive feedback can result in a current controlled negative resistance. The necessary conditions are discussed. The electron temperature approximation is used to show that the screening model does indeed show the qualitative features of the observed negative resistance. A numerically calculated electron distribution function is used for a quantitative comparison of theory and experiment in *n*-type GaAs. The agreement is good. The screening model is also used to show how high photocurrent multiplication can be obtained in a sample undergoing impact ionization.

1. INTRODUCTION

A CURRENT controlled negative resistance (CCNR) was first observed by McWhorter and Rediker[1] at low temperatures in compensated Ge and has since been observed in other doped semiconductors[2]. The CCNR does not depend on electrical contacts but is a property of the bulk crystal. This phenomenon, which is associated with impact ionization of shallow donors or acceptors, requires a compensated material. The significant feature is that the current voltage curve is *S* shaped; see Fig. 1.

Several models[3-6] have been proposed to explain the CCNR. McWhorter and Rediker[3] postulated that filled and unfilled donor pairs formed a configuration analogous to the hydrogen molecule ion. This configuration is an important energy loss mechanism until impact ionization removes the electron. Yamashita[4] assumed that a mutual interaction between the conduction electrons and the impurity system would keep the two systems at the same electron temperature. The electrons would thus lose energy to the lattice via the impurity system. Once impact ionization begins, the impurity system is no longer effective as an energy loss mechanism

and the electron temperature rises producing a negative resistance. Zylbersztein[5] speculated that free carrier scattering by carriers in an impurity band could lead to a negative resistance. All the above models, however, have the drawback that they require assumed interactions or configurations that have not been experimentally verified. Kurosawa[6], on the other hand, considered electron energy loss due to excitation of donor electrons to a bound state. He found that this process coupled with a change of shape of the distribution function due to electron-electron scattering could produce a CCNR.

In this paper we propose a new model for the CCNR; namely, screening of the electron-phonon and electron-impurity interactions. This model has the advantage that the parameters can be determined experimentally. In the next section we give a general discussion of the effects of screening on hot electron phenomena. We then use the electron temperature model to show qualitatively how electron screening leads to a CCNR. In the third section we shall make a quantitative comparison with observations of a CCNR in GaAs. Finally, we discuss the effects of changing the carrier density by light.

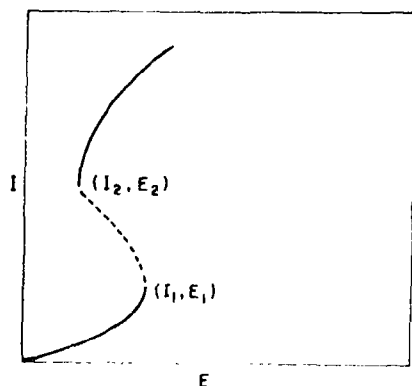


Fig. 1. A sketch of the current I vs. the electric field E showing a CCNR. The dashed portion of the curve is the negative resistance region bounded by the fields E_1 and E_2 .

2. MODEL

Negative resistance phenomena of the kind that we are concerned with in homogeneous substances are associated with hot electron* effects. The condition usually considered necessary for the CCNR is impact ionization; i.e. a high energy conduction band electron excites an electron from a state in the forbidden gap to the conduction band. Since both electrons remain in the conduction band, this process leads to an increase in the current. Impact ionization leads to a precipitous increase in carrier density with increasing electric field that may or may not lead to a CCNR. In fact, we shall show that, for the CCNR to occur, the increase in carriers due to impact ionization must increase the impact ionization probability.

In our model of the CCNR, the increased carrier density increases the screening of the scattering potentials. Thus, the electron scattering decreases leading to an increase in the average electron energy. The hotter electrons cause more impact ionization, generating more carriers and making the distribution still hotter. Therefore, a high

rate of impact ionization can be sustained at a value of electric field that is lower than that required for impact ionization at low carrier density.

The straightforward method of showing that a CCNR exists would be to solve the Boltzmann transport equation and from its solution calculate the field dependence of the current. The Boltzmann equation would contain, in addition to the usual terms representing electron-phonon, electron-electron and electron-impurity scattering, terms representing electron-impurity recombination and ionization of neutral impurities. This equation is a nonlinear integro-differential equation which is virtually impossible to solve exactly. Even a numerical approximation would be a costly undertaking. Therefore, we shall adopt an alternative procedure that uses an approximation to the exact Boltzmann equation.

Physically we expect the scattering of electrons from charged impurities and other electrons to be the most frequent collision processes followed closely by electron-phonon collisions. These three processes have the following roles: the first determines the asymmetric part of the distribution function and hence the power input to the electron gas. The second tends to redistribute the energy among the electrons and bring them to a common temperature, while the third exchanges energy with the lattice. We expect these processes to be much more frequent than those in which the density of conduction electrons n changes. Thus it is reasonable to imagine that n is fixed, then solve the Boltzmann equation neglecting those interactions that change the density of conduction electrons. One obtains as a solution an energy ϵ dependent distribution function $f(n, \epsilon, E)$, in which n as well as the electric field E appear as parameters. The carrier density is then determined by calculating, with the aid of $f(n, \epsilon, E)$, the rates of excitation and recombination, both of which depend explicitly on n . The physical configura-

*In this paper we refer to an n -type semiconductor. The arguments apply equally well to a p -type semiconductor.

tion is the steady state for which n does not change. By equating rates of ionization and recombination one obtains a further condition which determines the value of n .

In more detail then, the rate equation is:

$$\frac{dn}{dt} = (nW_I + W_E)(N_D - N_A - n) - nW_R(N_A + n), \quad (1)$$

where

$$nW_I = \int_0^\infty \epsilon^{1/2} f(n, \epsilon, E) \omega_i(n, \epsilon) d\epsilon \quad (2)$$

and

$$nW_R = \int_0^\infty \epsilon^{1/2} f(n, \epsilon, E) \omega_r(n, \epsilon) d\epsilon. \quad (3)$$

We consider an n -type semiconductor with a spherical parabolic conduction band and N_D donors and N_A acceptors. Electronic transitions take place from the donor level to the conduction band due to impact ionization, thermal excitation, and photoexcitation. Transitions take place from the conduction band to the donor level accompanied by emission of photons or by impact recombination. The thermal and photoexcitation rates are proportional to the number of unionized donors, but otherwise insensitive to the electron distribution. Impact ionization and recombination with the emission of a phonon or photon are linear in the electron distribution function and thus implicitly proportional to the number of conduction electrons. This dependence is written explicitly in equations (2) and (3). Impact recombination is quadratic in n and is small for low electron densities. We shall therefore neglect it. The functions $\omega_r(n, \epsilon)$ and $\omega_i(n, \epsilon)$ are the transition probabilities for electron-donor recombination and donor impact ionization, respectively. These quantities are functions of n because of the dependence of the interactions on screening. The remaining excitation probability W_E is the sum of the thermal and the photoexcitation probabilities. The terms $(N_D - N_A - n)$ and $(N_A + n)$ are the populations of neutral and ionized donors, respectively.

In principle the rate equation can be solved for n . Then the current can be determined from the equation

$$I = neV, \quad (4)$$

where V is the electron drift velocity and e the electron charge. The Boltzmann equation is used to find V which is in general a function of n and E . In practice, however the dependence on n of W_I and W_R is so complicated that the rate equation can only be solved numerically. Therefore, we shall not attempt to calculate the current in full but shall content ourselves with showing that the screening model does give a CCNR. We shall do this by showing that the turning points (I_1, E_1) and (I_2, E_2) of the characteristic curve in Fig. 1 are indeed present.

In Fig. 1 the current vs. electric field curve shows a CCNR, which is bounded by the fields E_1 and E_2 . Even though this curve shows I as a function of E , it is sometimes convenient for the discussion that follows, to view E as a function of I . The CCNR region is defined by a negative dI/dE (dashed portion of the curve). Tracing the current field curve from the ohmic region to E_1 , we see the slope is positive at currents below I_1 . At I_1 , dE/dI passes continuously through zero. As a function of E , I is double valued, and for the lower and upper branches, dI/dE goes to plus and minus infinity, respectively. Between the current values I_1 and I_2 , dE/dI is negative. In this region of negative resistance, the system is unstable. From the above, we see that a necessary and sufficient condition for the CCNR is that dE/dI decreases continuously through zero with increasing I . The values of E and I for which this occurs locate the first turning point. Naturally, dE/dI must eventually increase to positive values again. The second turning point is located when it again passes through zero. We first find dI/dE and invert it to find dE/dI . To find dI/dE we proceed by differentiating equation (4) with respect to E . Remembering

that V , as calculated from the solution of the Boltzmann equation is a function of both N and E and that n calculated from the supplementary rate equation is a function of E only, we can write

$$\frac{dI}{dE} = e(V + n \frac{\partial V}{\partial n}) \frac{dn}{dE} + en \frac{\partial V}{\partial E}. \quad (5)$$

If any of the derivatives on the right hand side of equation (5) were infinite, dE/dI would be zero. A situation where $\partial V/\partial E$ is infinite has not been observed experimentally; we shall therefore restrict our calculation to situations where $\partial V/\partial E$ is positive and finite. Thus we must find an expression for dn/dE that becomes infinite at the critical fields E_1 and E_2 .

For this purpose we can use the rate equation, (equation (1)), which is a function of both n and E . By taking the derivative of this equation on the curve $dn/dt = \dot{n} = 0$, we can write

$$\frac{dn}{dE} = - \frac{\partial \dot{n} / \partial E}{\partial \dot{n} / \partial n}. \quad (6)$$

The condition, $\dot{n} = 0$, defines the steady state. Explicitly, at the first turning point we shall find that

$$\frac{\partial \dot{n}}{\partial n} \propto (n(E) - n_1) \quad (7a)$$

where the fact that n is a function of E along the characteristic curve determined by $\dot{n} = 0$ is indicated by writing n as a function of E . Since $\partial \dot{n} / \partial E$ is slowly varying in the vicinity of E_1 , which is defined by $n(E_1) = n_1$, we can write equation (6) as

$$\frac{dn}{dE} = \frac{-C_1}{(n(E) - n_1)}. \quad (7b)$$

The constant C_1 depends on the material parameters but not on E . This form is good only in the immediate vicinity of E_1 . Integrating we find that

$$(n(E) - n_1)^2 = 2C_1(E_1 - E) \quad (7c)$$

which is the desired form for a CCNR. Similar considerations apply to the second turning point (E_2). Thus we shall concentrate our attention on finding an expression for $\partial \dot{n} / \partial n$ and showing that it has the form of equation (7a) at the turning points.

The partial derivative $-\partial \dot{n} / \partial n$ can easily be calculated from equation (1) to give

$$\begin{aligned} -\frac{\partial \dot{n}}{\partial n} = & n(W_I + W_R) + W_E \frac{N_D}{n} (1 - K) \\ & - nN_D \left[(1 - K) \frac{\partial W_I}{\partial n} - \left(K + \frac{n}{n_D} \right) \frac{\partial W_R}{\partial n} \right], \end{aligned} \quad (8)$$

where K is the compensation ratio N_A/N_D . We have used the property that $\dot{n} = 0$ to simplify this equation.

If W_I and W_R are independent of n , then $-\partial \dot{n} / \partial n$ is positive and the slope dI/dE is positive. Therefore, there is no negative resistance. Thus impact ionization is not a sufficient condition for a CCNR. The change in the carrier density must also affect the rate of impact ionization or recombination, either through the distribution function or via the transition probabilities. As we shall show, it is the effect of the carrier density on the distribution function that is dominant in producing the CCNR.

To show if a CCNR can occur, we must evaluate W_I and W_R . This requires a solution of the Boltzmann equation for $f(n, \epsilon, E)$. Only numerical solutions are possible for the interactions that are present in most semiconductors[7]. These include ionized and neutral impurity scattering, electron-electron scattering, and electron-phonon scattering. Thus we shall use the familiar electron temperature model[8] for the distribution function. This model is justified in the event that electron-electron scattering is more frequent than electron-phonon scattering. Then the electron distribution can be described by an electron temperature T^* which is

higher than the lattice temperature. In this model the symmetric part of the distribution function is assumed to be a Maxwellian with a temperature T^* . The Boltzmann equation, omitting electron-electron scattering, is then used to find the asymmetric part of the distribution function and hence the drift velocity. The Boltzmann equation is supplemented by a rate equation describing the energy flow between field, electrons, and lattice. That is, the electron temperature is determined by equating the rate of energy gain from the field to the energy loss rate to the lattice. Just as before we dropped the n changing interactions from the Boltzmann equation and then regarded n as a fixed parameter, we now drop the electron-electron interactions and regard the electron temperature as a fixed parameter. The electron temperature model is sufficient for qualitative arguments. In comparison with experiment, a numerical solution of the approximate Boltzmann equation will be used.

Assuming that T^* has been determined, we proceed to calculate the functions W_R and W_I by equations (2) and (3). The distribution function can be written as

$$f(n, \epsilon, E) \propto n(T^*)^{-3/2} \exp(-\epsilon/kT^*). \quad (9)$$

The actual form of the transition probabilities $\omega_i(n, \epsilon)$ and $\omega_r(n, \epsilon)$ are complicated. For

$$F = \frac{(KN_D/n + 1)(1 - K - n/N_D)}{1 + [(KN_D/n + 1)(1 - K) + 1 - K - n/N_D]W_E/nW_I} \quad (12)$$

our qualitative discussion, we shall use mathematically simplified, but physically reasonable expressions for these functions. The impact ionization probability is zero for energies less than the ionization energy ϵ_i . For energies greater than ϵ_i , the energy dependence of the transition probability is weak compared with the exponential energy dependence of the distribution function. Thus we may approximate $\omega_i(n, \epsilon)$ by a constant for $\epsilon > \epsilon_i$. Similarly, we have

neglected screening in determining the form of $\omega_r(n, \epsilon)$ since any screening terms are unimportant compared with the exponential form of $f(n, \epsilon, E)$. In other words, the effect of screening on the distribution function is much more important than the effect of screening on the impact ionization probability. Because of the threshold nature of the impact ionization, it will dominate in determining the carrier density and we may, for simplicity, replace $\omega_r(n, \epsilon)$ by a constant.

It is now straightforward to calculate the excitation probabilities that occur in the rate equation. For the impact ionization probability we have

$$W_I \propto (\epsilon_i/kT^*)^{1/2} \exp(-\epsilon_i/kT^*), \quad (10)$$

for the condition that $\epsilon_i \gg kT^*$. This condition is satisfied for the cases of interest. Here the n dependence of W_I is through the n dependence of T^* . The recombination probability W_R is a constant and thus independent of T^* and n .

Since we are only interested in the term that is zero at the critical field for the CCNR, we can write

$$\frac{\partial \dot{n}}{\partial n} \propto -[1 - (\epsilon_i/kT^* - 0.5)F \frac{\partial T^*}{\partial n} \frac{n}{T^*}], \quad (11)$$

where the function F is positive and given by

Since $\epsilon_i/kT^* > 1$, equation (11) shows that, for a CCNR to occur, the electron temperature must be a function of n and moreover an increasing function of n . Of course screening is not the only mechanism that can give a positive $\partial T^*/\partial n$. Any process that causes the scattering to decrease when n increases will give a positive $\partial T^*/\partial n$.

Returning now to the twice truncated Boltzmann equation, let us specialize the physical system to take advantage of a solu-

tion available in the literature[9]. We consider that the mobility is determined by ionized impurity scattering and the energy loss is to acoustic phonons interacting via the deformation potential. This situation closely approximates the low temperature electron transport in germanium. Also, for these two interactions, the electron temperature model gives a distribution that resembles the one calculated from a solution of the Boltzmann equation[7]. For ionized impurity scattering the drift velocity can be written as

$$V = EV_0(T^*)^{1/2}/(N_I + n)g(\zeta), \quad (13)$$

where

$$\zeta = a(T^*)^2/n \quad (14)$$

and

$$g(\zeta) = \ln(1 + \zeta) - \zeta/(1 + \zeta). \quad (15)$$

Equation (13) is just the Brooks-Herring expression[10] for the drift velocity. The constants a and V_0 are positive. The density of ionized impurities when $n = 0$ is N_I . In the expression for ζ , the usual approximation has been made of replacing ϵ by $3kT^*$. Equating the power input ($neVE$) to the power lost to the phonons gives the following equation for the electron temperature.

$$(N_I + n)(1 - t^{-1})g(\zeta) = CV_0E^2 \quad (16)$$

where $t = T^*/T$ and C is a positive constant.

Inclusion of screening of the electron-phonon interaction, would enhance the possibility of a CCNR, since, by itself it would lead to a positive $\partial T^*/\partial n$. Neglecting this mechanism leads to a simplification of the expressions that follow.

Using expression (16) we can readily write

$$\frac{\partial T^*}{\partial n} = \frac{T^*}{2n} \left(1 - \frac{Rn}{N_I + n} \right) / \left(1 + \frac{2R}{t-1} \right), \quad (17)$$

The function R is a slowly varying function of n and T^* that is given by

$$R = (1 + 1/\zeta)^2 g(\zeta). \quad (18)$$

Usually $\zeta \gg 1$ and thus $R > 1$. Equation (17) shows that $\partial T^*/\partial n$ is positive when $N_I \gg n$. When $n > N_I$, $\partial T^*/\partial n$ becomes negative. The sign of $\partial T^*/\partial n$ has a simple physical interpretation. If $n \ll N_I$, then the main effect of increasing the carrier density is to screen the ionized impurity interaction. Thus an increase in n decreases the scattering and increases T^* . If, however, $n \gg N_I$, then increasing n increases the density of ionized impurities. Therefore, the increased scattering more than compensates for the increased screening and T^* decreases with increasing n .

We now show that the dominant form of $\partial \dot{n}/\partial n$ at the turning points is $(n(E) - n_1)$. By using equations (12) and (17) we can in principal express equation (11) in this form; however, the expression for n_1 is cumbersome. Therefore, we make the following simplifying approximations that are valid for the cases where a CCNR is observed. We consider that $n/N_D \ll K$ and $t \gg 1$. For the first turning point (E_1, I_1) only, we also have that $n \ll N_I$ and $n^2 W_H/W_E N_D \ll 1$. Then equation (11) can be rewritten as

$$\frac{\partial \dot{n}}{\partial n} \propto (n(E) - n_1), \quad (19)$$

where

$$n_1 = \frac{4(1-K)^2 k^2 W_E}{K^2 W_H^2 \epsilon_i^2 a} \exp\left(\frac{eV_0 E_1^2}{N_I}\right). \quad (20)$$

Expression (20) was obtained with the aid of equations (1) and (16) using the condition that $\dot{n} = 0$. From equation (19) then we see that the first turning point (E_1, I_1) is of correct form for a CCNR. The second turning point (E_2, I_2) is given when $\partial \dot{n}/\partial n$ again passes through zero. In this case we have

$$\frac{\partial \dot{n}}{\partial n} \propto \left(\frac{N_I}{R-1} - n(E) \right). \quad (21)$$

This expression is also of the desired form. Here we see that the turning point arises because the density of electrons becomes the order of the density of ionized impurities

N_i . Thus it is the increase in impurity scattering that counteracts the screening and terminates the CCNR.

Lastly we show why a CCNR is not observed in an uncompensated sample. In this case $K = N_i = 0$ and there is no CCNR because $\partial T^*/\partial n$ is negative. This is readily seen from equation (17) when N_i is set equal to zero.

The above discussion shows that the screening model explains the general features of the CCNR that have been observed experimentally. In the next section we make a quantitative comparison with experiment.

3. COMPARISON WITH EXPERIMENT

To show how the above ideas can be applied, we analyze data obtained from low temperature Hall effect measurements made on

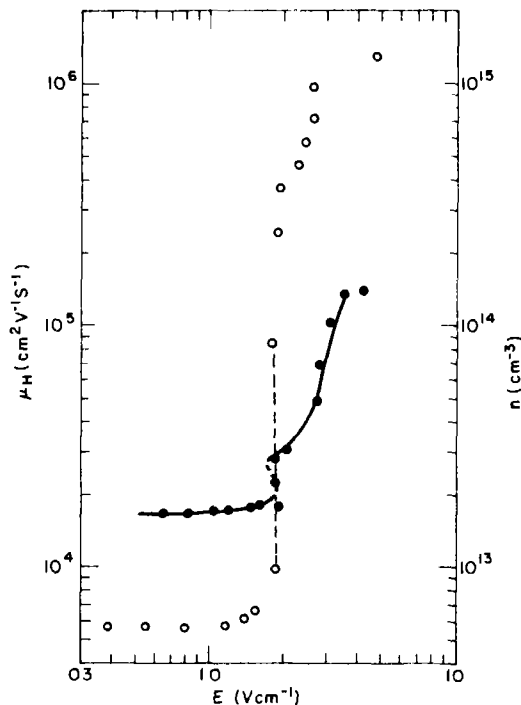


Fig. 2. Electric field dependence of the Hall mobility μ_H and carrier density n in n -type GaAs at 5.12°K . The open circles are carrier density; the dots are mobility. The solid curve is the calculated value of the mobility. The dashed curve shows the CCNR region.

n -type GaAs[11]. This material is high purity epitaxial GaAs which contains 1.3×10^{15} donors and 1.7×10^{14} acceptors. In Fig. 2 the Hall mobility μ_H and carrier density n at 5.12°K are plotted vs. electric field. The values of n were obtained from measured values of the Hall constant R_H using the approximate relation $n = (R_H e)^{-1}$. As can be seen from the low value of the carrier density at low electric field, the donors are deionized at low temperature. For this material, the donor binding energy is about 0.004 eV ($\sim 42^\circ\text{K}$).

The data shown in Fig. 2 are typical of a CCNR. At about 2 v/cm both n (open circles) and μ_H (dots) and thus I increase with decreasing electric field. The dotted line represents the region of negative resistance. This region, however, is not observed experimentally. Only the two turning points are observed. Thus we measured n and μ_H only at the beginning and end of the CCNR.

The solid curve in Fig. 2 is the Hall mobility calculated using the experimental values of n^* . In this material the momentum relaxation is dominated by strong ionized impurity scattering. The electron phonon interaction is only important as an energy loss mechanism. The dominant electron-phonon interaction for electrons whose energy is less than 0.009 eV [11] ($\sim 100^\circ\text{K}$) is via the piezoelectric interaction with acoustic phonons. For energies between 0.009 – 0.036 eV the deformation potential acoustic phonon interacting dominates. For higher energies the optical phonon dominates the energy loss. For the field region in which μ_H is calculated, the electrons that contribute to the electron transport have energies less than the optical phonon energy. Thus we need only consider the acoustic phonons. The procedure for calculating the electron distribution function

*No attempt was made to calculate n because we feel that the result would be model dependent. It would be easy to choose the unknown parameters in expressions for $\omega_c(n, \epsilon)$ and $\omega_i(n, \epsilon)$ so that the experimental data could be fitted.

is outlined in Ref.[7]. In the appendix of Ref.[11] the theory is extended to include screening of the electron-phonon interaction. The solid μ_H curve in Fig. 2 was calculated numerically using the above theory. For each value of the applied electric field, μ_H was calculated using the experimental value of n . A deformation potential of 7 eV and a piezoelectric stress constant of 2×10^9 V/M were used. The deformation potential is the value given by Ehrenreich[12]. The piezoelectric stress constant, which was chosen to give the best fit to the data, is 20 per cent larger than the accepted value[13]. The ionized impurity density was chosen equal to the number of acceptors and ionized donors.

On the theoretical curve for μ_H , the CCNR region is shown by a dashed curve. In this region μ_H was not calculated. The mobility was calculated at the beginning and end of the CCNR and the dashed curve is drawn in to connect these two points. The agreement between experiment and theory is quite good. It shows that screening can lead to a CCNR.

We should remark that if n is held fixed, then μ_H is a monotonically increasing function of E . This is equivalent to the statement that $\partial V/\partial n$ is positive and finite. The total derivative of V and similarly μ with respect to E does not, however, remain finite. This is because dV/dE contains dn/dE , which becomes infinite at the beginning of the CCNR. Thus showing that the mobility exhibits a CCNR is equivalent to showing that the current voltage curve exhibits a CCNR.

4. PHOTOCURRENT GAIN

As a final example of how screening affects the electron transport, we examine the behavior of the current when the carrier density is increased by photoexcitation. In this case the carrier density can be changed at constant electric field giving a degree of freedom that was not present in our earlier discussion.

We consider the situation where the term

W_E , which appears in equation (1), represents the excitation probability for light. In this case

$$W_E = W_i + hL, \quad (22)$$

where W_i is the excitation probability for thermal ionization, h is a constant, and L is the light intensity. Since we are interested in examining the electric field dependence of the photocurrent, it would be appropriate to solve the rate equation for n . However, as we noted earlier, this equation can only be solved numerically. Thus we adapt a procedure similar to the one used to give a criterion for a CCNR. We examine the slope of the n vs. L curve. This slope dn/dL is equivalent to the differential photoconductive gain (DPG). We then compare the DPG in the ohmic and non-ohmic regions to see how the electric field has affected the steady state photocarrier density*. The electric field has two effects. It can change the recombination kinetics; it can cause impact ionization. A decrease in the recombination probability will certainly increase the photocarrier density. An increase in the impact ionization probability, however, may not increase the photocarrier density[14]. We shall discuss below under what conditions impact ionization can be expected to increase the photocurrent density.

With the aid of the rate equation, we can now write the slope of the n vs. L curve at constant electric field as

$$\frac{dn}{dL} = -\frac{\partial \dot{n}}{\partial L} \frac{\partial \dot{n}}{\partial n}, \quad (23)$$

where the partial $\frac{\partial \dot{n}}{\partial L}$ is

$$\frac{\partial \dot{n}}{\partial L} = h(N_D - N_A - n). \quad (24)$$

Thus the effects of the electric field on the

*The DPG is, by definition, independent of field in the ohmic region.

slope dn/dL are determined by the partial derivative $\partial \dot{n}/\partial n$. This is the same partial derivative that determined the critical behavior of the n vs. E curve (see equation (6)). Thus we see the intimate connection between the CCNR and the effects of the electric field on the photocurrent.

We imagine that the electric field is at a value E_c which is between the fields E_1 and E_2 shown in Fig. 1 and that the current is at a value below I_2 , i.e. the positive resistance region. Now we increase the light intensity which increases the carrier density. At a critical carrier density, $-\partial \dot{n}/\partial n$ becomes zero. At this point the system switches to a high conductivity state compatible with the characteristic curve shown in Fig. 1. Remember that the system is at constant field. In this mode the system operates as a light activated switch. For the above discussion to apply, however, the previous considerations that permitted $\partial \dot{n}/\partial n$ to have a zero must still be met. If $\partial \dot{n}/\partial n$ does not have a zero, there can be no switching. Nevertheless, there still can be an increase in the DPG . This is because $-\partial \dot{n}/\partial n$ becomes very small. Thus DPG becomes very large. In fact, in the high conductivity, but positive resistance state, the DPG can be much greater than it was in the low conductivity state.

5. SUMMARY

In this paper we have shown that free carrier screening of the electron impurity and electron-phonon interactions coupled with impact ionization is sufficient to produce a current controlled negative resistance.

Using this model, we were able to calculate the field dependence of the Hall mobility in n -type GaAs and obtain good agreement with data that showed a current controlled negative resistance. We also showed how screening, accompanying impact ionization, can lead to photocarrier multiplication. When the semiconductor exhibits a negative resistance, then light can be used to switch the semiconductor from a low conductivity to a high conductivity state.

Acknowledgement—I am indebted to Dr. S. Freeman for a critical reading of the manuscript and helpful suggestions. I wish to thank Drs. L. Friedman and A. Rose for many stimulating conversations.

REFERENCES

1. McWHORTER A. L. and REDIKER R. H., *Proc. IRE* **47**, 1207 (1959).
2. REYNOLDS R. A., *Solid St. Electron.* **11**, 385 (1968), ANDO K., *J. phys. Soc. Japan* **21**, 1295 (1966).
3. McWHORTER A. L. and REDIKER R. H., *Proc. Int. Conf. Semiconductor Physics*, p. 134 Prague 1960 (Czechoslovak Academy of Sciences, Prague (1951)).
4. YAMASHITA J., *J. phys. Soc. Japan* **16**, 720 (1961).
5. ZYLBERSZTEJN A., *J. Phys. Chem. Solids* **23**, 297 (1962).
6. KUROSAWA T., *J. phys. Soc. Japan* **20**, 1405 (1965).
7. CRANDALL R. S., *Phys. Rev.* **169**, 585 (1968).
8. STRATTON R., *Proc. R. Soc. A* **242**, 355 (1957).
9. PAIGE E. G. S., *Progress in Semiconductors* (Edited by A. F. Gibson and R. E. Burgess), Vol. 8, Chap. 6, Wiley, New York (1964).
10. BROOKS H., *Adv. Electronics and Electron Phys.* (Edited by L. Morton) Vol. 7, pp. 156–160, Academic Press, New York, (1955).
11. CRANDALL R. S., *Phys. Rev. B*, **1**, 730 (1970).
12. EHRENREICH H., *Phys. Rev.* **120**, 1951 (1960).
13. CHARLSON E. J. and MOTT G., *Proc. IEEE* **51**, 1239 (1963).
14. CRANDALL R. S., *Appl. Phys. Lett.* **10**, 316 (1962).

EFFET DE VALENCE EN ELECTROMIGRATION DANS L'ARGENT

NGUYEN VAN DOAN

Section de Recherches de Métallurgie Physique Centre d'Etudes Nucléaires de Saclay, France

(Received 14 November 1969)

Résumé—Nous avons étudié la migration sous champ électrique de ^{110}Ag , ^{106}Cd , $^{114\text{m}}\text{In}$, ^{113}Sn et ^{124}Sb dans l'Argent. Les valences efficaces de ces différents éléments obéissent bien à la loi de variation en $z(z+1)$ prévue théoriquement.

A partir de la comparaison entre les résistivités de l'ion en position stable et en position de col, nous essayons d'étudier la variation de sa structure électronique et de prévoir qualitativement certaines corrections à apporter aux divers calculs théoriques des constantes de diffusion dans l'Argent.

Abstract—We have investigated the electromigration of ^{110}Ag , ^{106}Cd , $^{114\text{m}}\text{In}$, ^{113}Sn and ^{124}Sb in Silver. The effective valences of these elements are in good agreement with the theoretical dependence in $z(z+1)$.

From the comparison between resistivities of the ion in the lattice site and in the saddle point, we try to study the variation of its electronic structure and to predict qualitatively some corrections to be made to theoretical calculations of diffusion constants in Silver.

1. INTRODUCTION

DEPUIS de nombreuses années, on a constaté expérimentalement que le passage d'un courant électrique continu à travers un échantillon métallique provoquait une migration de ses composants soit vers l'anode soit vers la cathode [1, 2]. Ainsi quand on soumet un alliage initialement homogène à l'action d'un courant électrique, on observe une redistribution des composants de l'alliage qui devient inhomogène [3, 4]. Outre cet effet de redistribution, le passage du courant électrique provoque aussi un flux de lacunes qu'il est facile de mettre en évidence par les techniques habituelles [5–7].

Il est maintenant bien établi que les ions se déplacent sous l'effet de deux forces: —la force électrostatique qui résulte de l'action directe du champ électrique: $F_s = ZeE$ —et la force de friction F_e , engendrée par les chocs avec les porteurs de charge. Dans la plupart des cas où les porteurs de charge sont des électrons, cette force d'interaction ion–électron est de sens opposé à la précédente et de loin la plus importante.

La quantité mesurée dans ces expériences

est 'la valence efficace Z^* ' définie par la moyenne de ces forces au cours d'un saut:

$$Z^*eE = [F_s + F_e]_0^a.$$

Cette étude est importante du point de vue pratique (purification des métaux et des semi-conducteurs) et du point de vue théorique, car l'interaction entre l'ion considéré et les électrons de conduction peut nous renseigner sur la structure électronique de l'ion en 'position de col', c'est-à-dire l'ion à mi-chemin entre deux sites lacunaires. Nous verrons par la suite comment cette connaissance nous permettrait de prévoir certaines corrections à apporter aux divers calculs théoriques des constantes de diffusion.

2. METHODES EXPERIMENTALES

Pour déterminer expérimentalement la valence efficace Z^* , nous avons utilisé la méthode suivante, déjà décrite dans [11]. Une couche mince du traceur à étudier est déposée en sandwich entre deux cylindres d'Argent très pur (Johnson–Matthey). L'échantillon ainsi préparé est ensuite

relié aux électrodes par l'intermédiaire de deux lames d'argent très souples. L'électrode supérieure est mobile. Nous disposons d'un générateur capable de débiter un courant continu de 2000 amp. Le diamètre de l'échantillon est de l'ordre de 7 mm. La température est contrôlée à $\pm 2^\circ$ près grâce à deux thermocouples "Thermocoax" placés à quelques mm de la couche de traceur et reliés à un système de régulation. Tous nos essais ont été effectués sous argon purifié pour éviter toute évaporation de l'argent. Le temps de traitement varie entre quelques jours pour les traceurs rapides et deux semaines pour les traceurs les plus lents.

Nous pouvons illustrer l'échantillon après l'expérience par le schéma de la Fig. 1. Le traceur a diffusé suivant une distribution gaussienne; mais au lieu d'être centré sur l'interface initial de soudure, le maximum de cette distribution est déplacé d'une quantité x_m . Nous verrons au paragraphe suivant que l'interface de soudure représente en fait le référentiel mobile par rapport auquel ont été effectuées toutes nos mesures de déplacement. Pour cela, la position de l'interface est repérée optiquement par rapport à une extrémité de l'échantillon; quant à la courbe activité-pénétration, elle est déterminée par la méthode habituelle "sectionnement et comptage". Une méthode standard [12] permet de connaître avec précision la position du maximum de cette courbe. Sur les Figs.

2-4 nous reproduisons quelques courbes typiques relatives à l'électromigration de ^{109}Cd , ^{114m}In et ^{113}Sn dans l'Argent.

Détermination de D , T , Z^*

Connaissant le temps t_s et le coefficient de diffusion D_s relatifs à la soudure, le coefficient

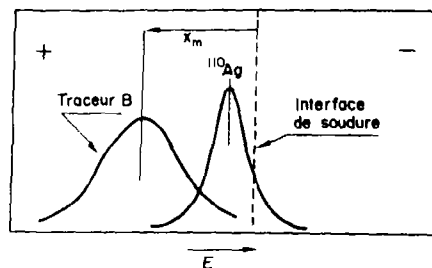


Fig. 1. Schéma de l'échantillon après l'expérience.

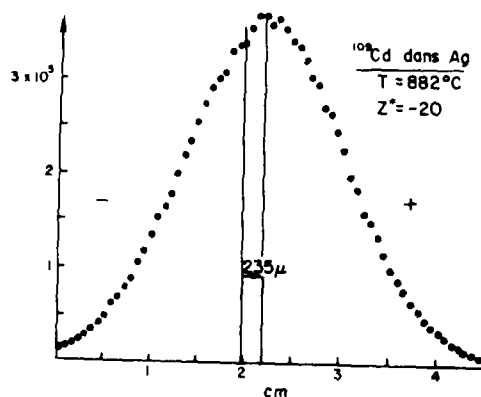


Fig. 2. Courbe typique de l'électromigration du ^{109}Cd .

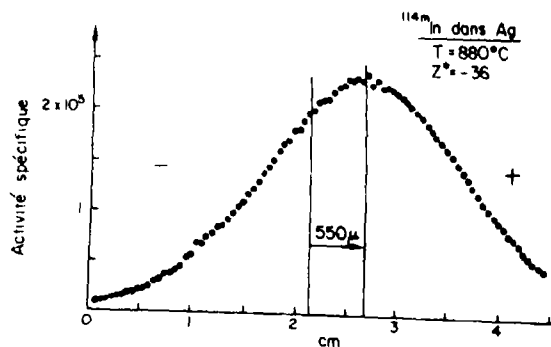
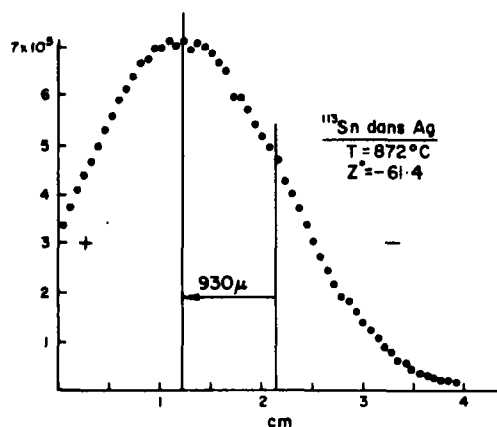


Fig. 3. Courbe typique de l'électromigration du ^{114m}In .

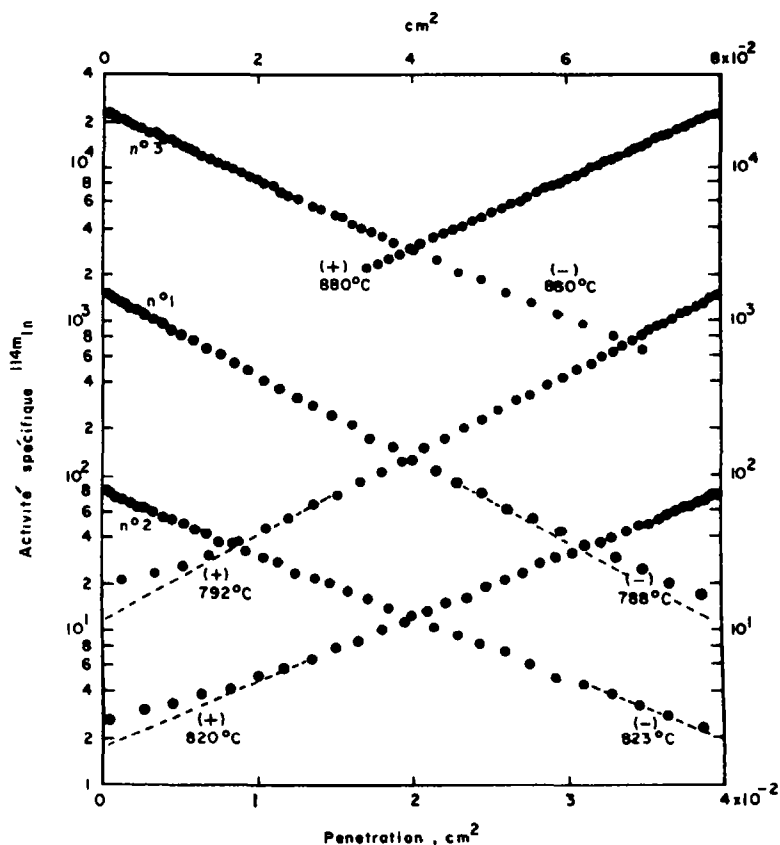

 Fig. 4. Courbe typique de l'électromigration du ^{113}Sn .

de diffusion et la température de l'expérience sont donnés par:

$$D = \frac{1}{4t} \left[\frac{1}{p} - 4D_0 t_s \right] \quad (1)$$

$$T = \frac{Q}{R \text{Log}(D_0/D)} \quad (2)$$

où p est la pente de la droite $\text{Log}(\text{activité spécifique})$ vs. $(x-x_m)^2$ Q et D_0 sont les constantes de diffusion données par [13]. Remarque—D'une façon générale, les pentes p_+ et p_- (Fig. 5) relatives aux côtés anodique et cathodique de l'échantillon sont égales


 Fig. 5. $\text{Log}(\text{activité spécifique})$ vs. Pénétration, + et - désignant respectivement les côtés anodique et cathodique de l'échantillon; l'échelle supérieure en abscisse est relative à la courbe Indium No. 3.

à 1 pour cent près. D'autre part, pour les expériences à des températures relativement basses (au-dessous de 800°C) nous constatons que l'activité spécifique du côté anodique est toujours supérieure à celle du côté cathodique, du moins pour une profondeur de pénétration assez grande, c'est-à-dire vers les régions où la diffusion dans les joints de grain est décelable.

La valence efficace Z^* est reliée au déplacement x_m par la relation de Nernst-Einstein:

$$x_m = \frac{DZ^*eE}{kT} \cdot t. \quad (3)$$

A l'aide de la loi d'Ohm: $E = \rho_0 J$ et de la relation (1) où $D_1 t_1$ est négligeable devant Dt , il vient:

$$Z^* = \frac{4\rho_0 kT x_m}{e\rho_0 J} \quad (4)$$

où la durée de l'expérience n'intervient pas explicitement. Les résultats obtenus sont groupés dans les tableaux 1 et 2.

3. PROBLEME DE REFERENTIEL ET RELATION ENTRE VALENCES EFFICACES

L'analyse phénoménologique [11, 14] nous donne le flux du traceur i par rapport au référentiel mobile du réseau:

$$J_i = D_i \frac{\partial n_i}{\partial x} + n_i D_i Z_i^* \frac{eE}{kT} \quad (5)$$

où $i=A$ ou B respectivement pour l'auto- et l'hétéro-diffusion. Ce référentiel mobile est aussi appelé 'référentiel de la vitesse atomique moyenne' que nous noterons R ; il peut être matérialisé dans nos échantillons par les traces de soudure que l'on révèle facilement par une attaque chimique [11].

Ainsi, avec nos conventions, le référentiel fixe R_0 du laboratoire sera repéré par le maximum de la distribution gaussienne d'un isotope A de la matrice (ici ^{110}Ag) (voir Fig. 1). Dans ce référentiel R_0 , les flux des traceurs A et B s'écrivent (Annexe):

$$J_1^0 = -D_1 \frac{\partial n_1}{\partial x}$$

$$J_n^0 = -D_n \frac{\partial n_n}{\partial x} + \frac{n_n e E}{kT} (Z_n^* D_n - Z_1^* D_1). \quad (6)$$

Ce qui montre que dans R_0 : (1) la valence efficace du traceur A est identiquement nulle, (2) celle du traceur B est égale à $(Z_n^* - D_1/D_n Z_1^*)$. Autrement dit, les valences efficaces données par les différentes théories citées plus haut sont définies implicitement dans le référentiel mobile R . C'est pour cette raison que toutes nos mesures de x_m ont été effectuées par rapport à l'interface de soudure.

Relation entre les valences efficaces

Le modèle théorique de Bosvieux et Friedel donne: — pour un atome de solvant:

Tableau 1. Electromigration dans l'Argent

Traceur No	t (sec)	J 10^5 (amp/cm ²)	D (cm ² /sec) 10^9	x_m (μ)	Z^*	$\pm \Delta Z^*$
^{109}Cd	1 8 577	4384.3	1.6	100	-22.02	2.5
	2 7 797	4054.6	4.49	220	20.41	1.5
	3 6 135	4501.4	5.61	235	-19.95	1.4
^{110m}In	1 11 412	3994.5	1.75	250	-41.39	2.4
	2 8 604	4164.5	3.13	320	-37.63	1.5
	3 5 94	4180.8	8.08	550	36.10	1.3
^{113}Sn	1 4 32	3475.4	0.40	30	-67.05	8.9
	2 2 592	3506.6	3.64	155	-61.92	4.4
	3 5 899	4299.8	7.86	930	-61.41	2.9
	4 6 39	3472.9	18.39	1850	-59.54	2.3

Tableau 2. Valences efficaces et résistivités résiduelles en $\mu\Omega\text{-cm/at}\%$

Traceur	T (°C)	Z*	$\Delta\rho^{(\text{stable})} + \Delta\rho^{(\text{col})}$	$\Delta\rho^{(\text{stable})}$ (Linde)
¹¹⁰ Ag [11]	833	-27.7	3.9	0
	867	-21.5	3.1	
	875	-19.9	2.9	
	889	-16.1	2.3	
¹⁰⁹ Cd	807	-22	3.0	0.38
	868	-20.4	2.94	
	882	-20	2.9	
	788	-41.4	5.62	1.78
^{114m} In	821	-37.6	5.27	
	880	-36.1	5.34	
	703	-67	8.40	4.32
	823	-62	8.76	
¹¹³ Sn	872	-61.4	9.10	
	932	-59.6	9.30	
	852	-102	14.9	7.26
	892	-95.8	14.5	
¹²⁴ Sb [11]	901	-95.1	14.5	
	933	-86.5	13.6	

$$Z_{\text{eff}}^* = -\frac{1}{2} Z \left[\frac{100}{\rho_0} \Delta\rho^{(z)} - (1 + f_0) \right] \quad (7)$$

où le 1er terme représente la force de friction, $\Delta\rho^{(z)}$ étant l'excès de résistivité dû à 1 pour cent d'atome de solvant en position de col; le 2^e terme représente la force électrostatique, f_0 traduisant la présence de la lacune proche voisine — pour un atome de soluté:

$$Z_{\text{eff}}^* = -\frac{1}{2} Z \left[\frac{100}{\rho_0} (\Delta\rho^{(z)} + \Delta\rho^{(z+Z)}) - (1 + f_0) \right] \quad (8)$$

où les deux termes en $\Delta\rho$ traduisent le fait que l'ion de soluté sent la force de friction à la fois en position stable et en position de col, les exposants (z) et $(z+Z)$ représentant les charges d'écran de l'ion dans ces différentes positions.

Si l'on suppose que l'excès de résistivité dû à un ion considéré est proportionnel au carré de sa charge d'écran [10], c'est-à-dire:

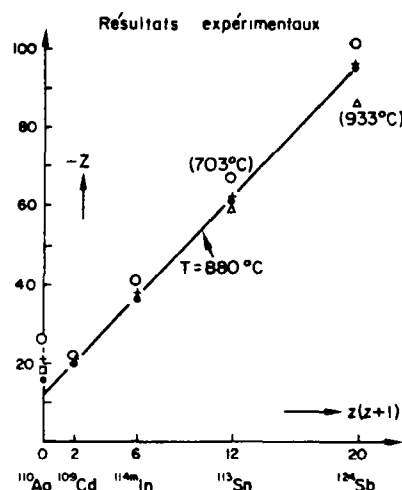
$$\begin{aligned} \Delta\rho^{(z)} &= \alpha z^2 \\ \Delta\rho^{(z+Z)} &= \alpha (z+Z)^2 \end{aligned} \quad (9)$$

il vient (pour l'Argent $Z = 1$):

$$Z_{\text{eff}}^* - Z_{\text{eff}}^* = c^{\text{re}} z(z+1) \quad (10)$$

z étant la différence de valence entre soluté et solvant.

Pour vérifier le modèle théorique et l'hypothèse faite ci-dessus, nous avons groupé tous nos résultats expérimentaux sur la Fig. 6 où nous avons représenté $-Z^*$ en fonction de $z(z+1)$, les différents points sont relatifs aux expériences faites à des températures différentes.

Fig. 6. Valences efficaces $-Z^*$ en fonction de $z(z+1)$.

Nous pouvons remarquer sur cette figure deux résultats importants: pour chaque élément, la valence efficace diminue lorsque la température augmente; pour une température donnée, par exemple vers 880°C, les points noirs représentant les valences efficaces de différents éléments sont sensiblement sur une droite.

Nous avons ainsi mis en évidence la dépendance de Z^* en $z(z+1)$, en parfait accord avec les prévisions théoriques précédentes, sauf peut-être pour l'Argent, là où les erreurs expérimentales sont les plus grandes à cause des déplacements relativement faibles [15].

4. DISCUSSION

Dans la suite de cet article, au lieu de la valence efficace, grandeur commode mais dont l'interprétation physique est difficile, nous allons plutôt nous intéresser à un paramètre plus familier: l'excès de résistivité qui est relié à Z^* par (7) ou (8) (Tableau 2).

Sur la Fig. 7, nous avons représenté: d'une part, les résultats de ce travail sur la courbe du haut, c'est-à-dire la somme des résistivités de l'atome en position stable et en position de col: $\Delta\rho^{(\text{stable})} + \Delta\rho^{(\text{col})}$, d'autre part, les valeurs expérimentales de Linde[16] relatives à la résistivité de l'atome en position stable sur la courbe du bas.

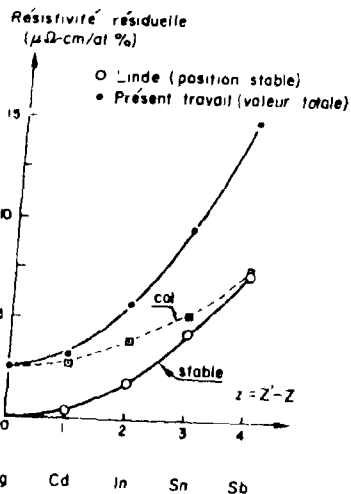


Fig. 7 Comparaison entre les différentes résistivités résiduelles.

D'où nous déduisons par différence la courbe du milieu relative à la résistivité de l'atome en position de col: $\Delta\rho^{(\text{col})}$.

Ce qu'il faut retenir de cette figure, c'est que $\Delta\rho^{(\text{col})}$ diffère d'autant plus de $\Delta\rho^{(\text{stable})}$ que le soluté est plus proche du solvant dans la classification périodique, à condition bien entendu de supposer que les $\Delta\rho^{(\text{stable})}$ diffèrent très peu des valeurs mesurées par Linde.

Avec cette hypothèse, nous pouvons décrire les courbes expérimentales de la

Fig. 7 par les relations suivantes (en $\mu\Omega\text{-cm/at.}\%$)

$$\Delta\rho^{(z)} = 0.45 z^2 \quad (\text{position stable}) \quad (11)$$

$$\Delta\rho^{(z+z)} = 0.21 z^2 + 0.66 z + 1.7 \quad (\text{-id-de col}) \quad (12)$$

$$\Delta\rho^{(z)} + \Delta\rho^{(z+z)} = 0.66 z(z+1) + 1.7. \quad (13)$$

Nous voyons donc que la relation (12) est différente de (9); cependant comme celle-ci elle conduit aussi à la même relation théorique (10) en $z(z+1)$.

Par ailleurs, on peut relier la résistivité résiduelle d'un défaut à sa structure électronique: autrement dit, un ion d'Antimoine possède dans l'Argent à peu près la même structure électronique dans les deux positions.

En conclusion, on peut dire donc de façon qualitative ceci: dans les calculs théoriques des constantes de diffusion, par exemple le calcul de l'énergie de migration ou celui de ΔQ par la théorie de Le Claire[17], on a supposé que le défaut quel qu'il soit a la même structure électronique dans les différentes configurations; or nous venons de voir que cette hypothèse est seulement valable pour les impuretés dont la valence est très différente de celle de l'Argent, comme l'Etain et l'Antimoine. Par contre pour l'autodiffusion et pour les impuretés telles que le Cadmium et l'Indium, on devrait avoir une contribution électronique due à la variation électronique lorsque l'ion passe de la position stable à la position de col.

Il serait intéressant de vérifier si cette propriété de la position de col est générale, c'est-à-dire si elle est encore valable dans d'autres matrices. Dans ce but, nous avons l'intention d'étudier la migration sous champ électrique de quelques impuretés dans l'Aluminium et d'évaluer ensuite l'ordre de grandeur de la contribution électronique dont on devrait tenir compte dans les divers calculs théoriques.

Remerciements — Nous tenons à remercier le Dr Y. Adda et Mr G. Brébec pour leurs précieux conseils et encouragements tout au long de ce travail. Nous remercions

également les Professeurs J. Friedel et H. B. Huntington pour l'intérêt qu'ils ont accordé à cette étude. Nos plus vifs remerciements vont aussi à Messieurs M. Bendazzoli et M. Sapin pour leur aide dans la mise au point de l'appareil et dans le comptage.

REFERENCES

1. SCHWARTZ K. E., *Elektrolytische Wanderung in Flüssigen und Festen Metallen*. Leipzig (1940).
2. HEUMANN T., *La Diffusion dans les Métaux*. Bibliothèque Technique Philips, Eindhoven (1957).
3. WILLIAMS J. M. and HUFFINE C. L., *Nucl. Sci. Engng* **9**, 500 (1961).
4. MOORE R. M. et al., *Trans. AIME* **233**, 1259 (1965).
5. SEITH W. and WEVER H., *Z. Elektrochem.* **57**, 891 (1953); **59**, 942 (1955).
6. WEVER H., *Z. Elektrochem.* **60**, 1170 (1956).
7. HUNTINGTON H. B. and GRONE A. R., *J. Phys. Chem. Solids* **20**, 76 (1961).
8. SKAUPY F., *Z. Phys.* **21**, 597 (1920).
9. FIKS V. B., *Fiz. tverd. Tela* **1**, 16 (1959).
10. BOSVIEUX C. et FRIEDEL J., *J. Phys. Chem. Solids* **23**, 123 (1962).
11. DOAN N. V. et BREBEC G., *J. Phys. Chem. Solids* **31**, 475 (1970).
12. GILDER H. M. and LAZARUS D., *Phys. Rev.* **145**(2), 507 (1966).
13. TOMIZUKA C. T. and SLIFKIN L., *Phys. Rev.* **96**(3), 610 (1954).
14. ADDA Y. et PHILIBERT J., *La Diffusion dans les Solides*. P. U. F. Paris (1966).
15. PATIL H. R. and HUNTINGTON H. B., *J. Phys. Chem. Solids* **31**, (1970).
16. LINDE J. O., *Annln. Phys.* **15**, 219 (1932).
17. LECLAIRE A. D., *Phil. Mag.* **7**, 141 (1962).

ANNEXE

Expressions de J_A^{0*} et J_B^{0*}

D'après [11] le flux des atomes de solvant s'écrit:

$$J_A = -D_A \frac{\partial n_A}{\partial x} + \frac{L_{A1}}{T} (z_A - z_A^*) \left(1 + \frac{L_{A1}}{L_{A1}^*} \right) eE \quad (\text{A.1})$$

(notation un peu différente de celle du texte où A désigne un isotope du solvant et non l'atome de solvant comme ici) et le flux des atomes de traceur ($i = A^*$ ou B):

$$\begin{aligned} J_i &= -D_i \frac{\partial n_i}{\partial x} + \frac{L_{ii}}{T} \left[(z_i - z_i^*) + \frac{L_{i1}}{L_{ii}} (z_1 - z_1^*) \right] eE \\ &= -D_i \frac{\partial n_i}{\partial x} + \frac{n_i D_i}{kT} Z_i^* eE \end{aligned} \quad (\text{A.2})$$

où:

$$Z_A^* = (z_A - z_A^*) \left(1 + \frac{L_{A1}^*}{L_{A1}^* A^*} \right) \approx \frac{1}{f_A} (z_A - z_A^*) \quad (\text{A.3})$$

$$Z_B^* = (z_B - z_B^*) + \frac{L_{BA}}{L_{BB}} (z_A - z_A^*) \quad (\text{A.4})$$

f_A étant le facteur de corrélation et égal à 0.78.

(1) Autodiffusion ($i = A^*$). D'après [14], nous avons:

$$J_{A^*}^0 = J_{A^*} + n_{A^*} V \quad (\text{A.5})$$

V étant la vitesse atomique moyenne:

$$V = -\frac{1}{n} (J_A + J_{A^*}) \text{ et } n = n_1 + n_{A^*} = c^{tr}.$$

Remplaçons J_A et J_{A^*} par (A.1) et (A.2), il vient:

$$-nV = \frac{L_{A1}}{T} (z_A - z_A^*) \left(1 + \frac{L_{AA^*}}{L_{AA^*}} \right) eE + \frac{n_{A^*} D_{A^*}}{kT} Z_A^* eE.$$

Or on sait que (p. 330 [14]):

$$L_{A1} + L_{AA^*} = \frac{n}{n_{A^*}} (L_{A^* A^*} + L_{AA^*}) = \frac{n}{n_{A^*}} \frac{L_{A^* A^*}}{f_A}.$$

D'où:

$$V = -\frac{D_{A^*} Z_A^* eE}{kT}. \quad (\text{A.6})$$

A l'aide de (A.2) et (A.6), l'équation (A.5) s'écrit:

$$J_{A^*}^0 = -D_{A^*} \frac{\partial n_{A^*}}{\partial x}.$$

(2) Hétérodiffusion ($i = B$). De même, nous avons:

$$J_B^0 = J_B + n_B V$$

où:

$$V = -\frac{1}{n} (J_B + J_A).$$

Si la concentration du traceur B est très faible $n_B \ll n$, on montre facilement que V a la même expression (A.6), il vient:

$$J_B^0 = -D_B \frac{\partial n_B}{\partial x} + \frac{n_B eE}{kT} (Z_B^* D_B - Z_A^* D_A).$$

STRUCTURE ELECTRONIQUE DES ALLIAGES A BASE DE METAUX DE TRANSITION ET DE METAUX NOBLES—II

CALCUL DE LA STRUCTURE ELECTRONIQUE DE L'ALLIAGE CuNi

R. RIEDINGER

Laboratoire de Physique des Solides, * Institut de Physique, 3, rue de l'Université,
Strasbourg, France

(Received 31 October 1969)

Résumé— Nous déterminons la structure électronique d'un alliage à base de métal noble ou de métal de transition. En supposant que dans la matrice les bandes 'd' sont bien représentées dans une approximation de liaisons fortes, et en négligeant l'hybridation s - d entre les bandes d et la bande de conduction 's', nous résolvons le problème d'une impureté dissoute dans la matrice par un développement en perturbation par rapport aux éléments de matrice $v_{\mathbf{k}}$ du potentiel d'impureté. Nous appliquons le formalisme dans le cas de l'alliage CuNi. Nous choisissons comme fonctions d'ondes de la bande de conduction des ondes planes orthogonalisées (OPW) et comme potentiel d'impureté un potentiel du type Yukawa $Z(e^{-\gamma r})/r$. Le paramètre γ est ajusté de manière à satisfaire la règle d'écran de Friedel. En accord qualitatif avec l'expérience nous obtenons un état lié virtuel, cependant la largeur de celui-ci est trop faible probablement parce que l'hybridation s - d de la matrice n'a pas été prise en compte.

Abstract— We study the electronic structure of noble metal or transition metal based alloys. We suppose that the 'd' bands are well described by the tight binding approximation; we neglect the s - d hybridization between s and d bands. We solve here the impurity problem by a perturbation development with respect to the matrix elements of the impurity potential between functions. We apply this formalism to the CuNi alloy. The wave functions of the conduction band are orthogonalised plane waves (OPW) and the impurity potential of Yukawa type $Z(e^{-\gamma r})/r$. The parameter γ is determined by the Friedel sum rule. In agreement with the experimental data we obtain a virtual bound state, but level is too narrow because no account has been taken of the hybridization in the pure metal.

1. INTRODUCTION

DANS un article précédent [1], nous avons étudié de façon générale la structure électronique des alliages à base de métaux nobles et de métaux de transition. Nous avons utilisé un modèle simplifié négligeant l'hybridation s - d dans la matrice; nous avons recherché les conséquences de la diffusion (ss , sd , dd) introduite par un potentiel de chaque impureté. Nous avons pu étendre le formalisme utilisant les déphasages dans le cas particulier où les fonctions d'onde 's' sont simplement des ondes planes modulées par les fonctions de bas de bande; nous avons précisé l'influence

des termes s - d et s - s sur les propriétés physiques des alliages à base de métaux nobles (résistivité électrique, variation de densité électronique...).

Dans cet article, nous voulons étendre le travail en calculant a priori de façon self consistante, et dans une approximation du type Hartree-Fock, la structure électronique d'alliages à base de métaux nobles et, en particulier, de l'alliage CuNi. Pour cela nous résolvons d'abord [1] le problème de la structure électronique des alliages à base de métaux nobles et de transition en faisant un développement en perturbation par rapport aux éléments de matrice $v_{\mathbf{k}}$, du potentiel d'impureté entre fonctions d'onde s ; nous

*Equipe de Recherches Associée au CNRS (n°100).

faisons les hypothèses suivantes: (1) les bandes d sont traitées en liaisons fortes, (2) l'hybridation s - d dans la matrice est négligée. Cette dernière hypothèse n'est qu'une première approximation dont les conséquences sont en cours d'étude.

Pour simplifier l'exposé, nous avons présenté le formalisme dans le cas de deux bandes seulement, une bande d , et une bande s , perturbées par un potentiel d'impureté localisé sur le site de l'impureté. L'extension au cas de cinq bandes d est triviale; elle est analogue à celle qui est présentée dans la référence [1].

Nous appliquons ensuite, ce modèle au calcul self consistant de la structure électronique d'alliages à base de métaux nobles, en particulier de l'alliage CuNi. Nous supposons que les fonctions d'onde ' s ' sont bien représentées par des fonctions d'onde plane orthogonalisées (OPW). Cette hypothèse n'est qu'une première approximation; les conséquences de ce terme d'hybridation sont actuellement en cours d'étude. Pour calculer la structure électronique de l'impureté, nous avons supposé que le potentiel d'impureté était du type Yukawa, sa portée étant fixée de façon autocohérente par la règle de Friedel [3]. En accord avec les résultats expérimentaux [2] nous obtenons, pour l'alliage CuNi, un état lié virtuel très étroit ($2\Delta \approx 0.2$ eV) centré en dessous du niveau de Fermi. La comparaison des résultats obtenus avec l'expérience (chaleur spécifique, résistivité électrique) semble cependant, montrer que cette largeur est trop faible. Nous attribuons ce désaccord quantitatif à l'influence de l'hybridation s - d dans la matrice.

Après avoir rappelé le formalisme utilisé (Section 1(1)) nous développons une solution des équations de Slater-Koster utilisant un développement en série par rapport aux éléments de matrice du potentiel d'impureté V entre fonctions d'onde s V_s^s . Nous utilisons ce développement parce qu'il est très rapidement convergent au voisinage des énergies de l'état lié virtuel (Section 1(2)); dans le

calcul explicite, nous n'utiliserons que le premier terme de ce développement. Dans cette hypothèse, nous donnons l'expression de la charge déplacée par l'impureté (1-3).

Dans la seconde partie de ce travail, nous discutons le cas spécifique de l'alliage CuNi. Nous présentons les hypothèses du calcul de la structure électronique de l'impureté (Section 2(1)). Nous discutons les résultats obtenus pour le potentiel s - d V_d^s ainsi que l'influence des termes s - s sur la forme et la position de l'état lié virtuel (Section 2). Enfin, dans la Section 2(3), nous comparons les résultats obtenus théoriquement aux résultats expérimentaux. Le calcul que nous présentons n'est que préliminaire parce qu'il suppose un grand nombre d'hypothèses simplificatrices sur la structure de bandes du métal pur (cf. Section 2(1)); nous pensons l'étendre à un cas où la structure de bandes du métal pur sera traitée de façon plus détaillée.

(1) Généralités sur le problème de la diffusion dans les métaux nobles

Nous résolvons le problème de la structure électronique des alliages de métaux nobles à l'aide d'équations du type Slater-Koster [4]. Nous supposons que les bandes ' d ' sont traitées dans l'approximation des liaisons fortes. Les fonctions d'onde ' d ' ont alors la forme suivante:

$$|d\mathbf{k}\rangle = \sum_{m=1}^5 a_m^{d\mathbf{k}} |dm\mathbf{k}\rangle \quad (1a)$$

N est le nombre d'atomes du système; les fonctions $|dm\mathbf{k}\rangle$ sont des fonctions de Bloch construites à partir des orbitales atomiques centrées sur les sites $\mathbf{R}_\lambda$, $|dm\lambda\rangle$:

$$|dm\mathbf{k}\rangle = N^{-1/2} \sum_{\lambda} e^{i\mathbf{k}\cdot\mathbf{R}} |dm\lambda\rangle. \quad (1b)$$

Les fonctions d'onde s seront notées $|s\mathbf{k}\rangle$; dans ce paragraphe, nous ne supposons rien sur leur forme particulière. Nous supposons que l'approximation des électrons

indépendants est valable, le potentiel d'impureté étant le même pour tous les électrons: l'hamiltonien de chaque électron dans le système constitué par le métal pur et une impureté à l'origine s'écrit alors:

$$H = H_0 + V \quad (2)$$

où H_0 est le hamiltonien du métal pur et V le potentiel d'impureté.

Nous noterons les éléments de matrice de l'opérateur de Green, G , défini par:

$$(E^+ - H)G = 1 \quad (E = E + i0) \quad (3)$$

sous la forme suivante:

$$G_{n'k'}^{nk} = \langle n'k' | G | nk \rangle. \quad (4)$$

En développant H sous la forme [2], les éléments de matrice satisfont le système d'équations suivant:

$$(E - E_{nk'})G_{n'k'}^{nk} = \delta_{nn'}\delta_{kk'} + \sum_{mk_1} \langle nk' | V | mk_1 \rangle G_{mk_1}^{nk} \quad (5)$$

$n, n', m = s$ ou di .

Dans la formule (5) E désigne l'énergie des fonctions de Bloch $|nk\rangle$ ($n = s, di$) du métal pur; la sommation sur les vecteurs k est effectuée dans la première zone de Brillouin lorsqu'ils sont associés à une bande di , dans tout l'espace réciproque lorsqu'ils sont associés aux bandes de conduction.

Le fait que les bandes 'd' puissent être représentées par (1a, 1b) permet de simplifier les équations (5): les éléments de matrice du potentiel d'impureté

$$\langle nk' | V | mk \rangle = N^{-1} v_{nk'}^{mk} \quad (6)$$

se mettent en effet sous la forme d'une somme d'un produit d'une fonction de k par une fonction de k' ,

$$\sum_{\alpha} f_{\alpha}(k) g_{\alpha}(k'); \quad (7)$$

le noyau de l'équation intégrale (5) est alors

dégénéré et, (5) est immédiatement soluble [1]. Nous précisons ci-dessous la forme des éléments de matrice (6):

$$v_{nk'}^{dk} = \sum_{m=1}^5 \sum_{\lambda} a_m^{dk} e^{ikR_{\lambda}} v_{nk'}^{m\lambda} \quad (8)$$

$$v_{nk'}^{m\lambda} = \sqrt{N} \langle sk' | V | m\lambda \rangle \quad (9)$$

$$v_{dk'}^{dk} = \sum_{m,m'=1}^5 \sum_{\lambda\lambda'} \langle m'\lambda' | V | m\lambda \rangle \times a_m^{dk} a_{m'}^{dk'} e^{-ik'R_{\lambda'}} \quad (10)$$

Nous avons étudié de façon générale les équations (5) à (10) dans l'article [1]; nous nous limitons ici à un modèle à deux bandes (sd) [17] dans le cas d'un potentiel perturbateur localisé. Les conséquences de la première hypothèse sont probablement négligeables. Nous considérons la diffusion des électrons s avec cinq bandes 'd' supposées indépendantes. L'écart introduit dans la structure électronique de l'impureté par le couplage entre bandes 'd' semble négligeable ainsi que le montrent les études sur les alliages à base de métaux de transition [5]. Les équations (5) à (10) peuvent d'ailleurs se résoudre de la même façon que ci-dessous; les calculs numériques, seuls seront plus complexes. La seconde hypothèse peut être vérifiée a posteriori lorsque le potentiel d'impureté aura été déterminé de façon autocohérente.

Elle est raisonnable pour les alliages du type CuNi. Le système (5) et (8) se met alors sous la forme simplifiée suivante:

$$(E - E_{sq}) G_{sq}^{sk} = \delta_{sq} + N^{-1} \left(v_{sq}^d \sum_{k_0} G_{dk_0}^{sk} + \sum_{k_0} v_{sq}^{sk_0} G_{sk_0}^{sk} \right) \quad (a)$$

$$(E - E_{dq}) G_{dq}^{sk} = N^{-1} \left(v_{dq}^d \sum_{k_0} G_{dk_0}^{sk} + \sum_{k_0} v_{dq}^{sk_0} G_{sk_0}^{sk} \right) \quad (b)$$

$$(E - E_{dq})G_{dq}^{dk} = \delta_{dq} + N^{-1} \left(v_d^d \sum_{k_0} G_{dk_0}^{dk} + \sum_{k_0} v_d^{k_0} G_{dk_0}^{dk} \right) \quad (c)$$

$$(E - E_{iq})G_{iq}^{dk} = N^{-1} \left(v_q^d \sum_{k_0} G_{dk_0}^{dk} + \sum_{k_0} v_q^{k_0} G_{dk_0}^{dk} \right) \quad (d)$$

(11)

Dans (11), $v_d^d = \langle d0 | V | d0 \rangle$

(2) *Principe d'une solution des équations de diffusion; potentiel effectif dans la bande 's'*

Nous nous proposons de résoudre le système (11) à partir de l'idée physique suivante. Les éléments de matrice v_d^d et v_d^s déterminant l'existence d'un état lié virtuel; le modèle d'Anderson pour les états liés virtuels correspond à une telle hypothèse [6]. Pour des énergies au voisinage de celles de l'état lié virtuel, la diffusion $s-d-s$ est résonante et, il apparaît raisonnable de négliger en première approximation le terme v_s^s . Nous obtiendrons aisément une solution des équations (11) à l'aide d'un développement en série par rapport aux éléments de matrice v_s^s : ce développement sera très rapidement convergent pour $E \sim E_l$ (E_l position de l'état lié virtuel).

Nous pouvons préciser ceci en introduisant un potentiel effectif v_{sq}^{sk} pour les électrons 's', compte tenu de la diffusion (sd) et (dd). En effet, en effectuant la somme $\sum_{k_0} G_{dk_0}^{dk}$ à partir de (11b) et en substituant dans (11a) nous obtenons pour la partie ss de la fonction de Green, G_{sq}^{sk} l'équation suivante:

$$G_{sq}^{sk} = \frac{1}{E - E_{dq}} \delta_{kq} + N^{-1} \times \sum_{k_0} \left(v_{sq}^{k_0} + \frac{G^{dd}(E)}{1 - v_d^d G^{dd}(E)} \right) \times v_d^{k_0} v_{k_0}^{sk} \quad (12)$$

où $G^{dd}(E)$ est défini par:

$$G^{dd}(E) = N^{-1} \sum_k \frac{1}{E^+ - E_{dk}} \quad (13)$$

Les équations (12) sont identiques aux équations donnant G_{sq}^{sk} , dans un alliage dont la matrice correspondante présente une seule bande s , le potentiel d'impureté $V^{(e)}$ ayant pour éléments de matrice:

$$v_q^{(e)k} = v_{sq}^{sk} + \frac{G^{dd}(E)}{1 - v_d^d G^{dd}(E)} v_d^q v_{sk}^d \quad (14a)$$

les bandes 'd' d'un métal noble étant pleines, le potentiel $v_q^{(e)k}$ conditionne à lui seul la variation de densité électronique autour de l'impureté, la résistivité électrique etc. Nous avons ainsi éliminé la bande 'd'. La diffusion due à $v^{(e)}$ est résonante au voisinage du pôle E_l de (14) défini par:

$$1 = v_d^d G^{dd}(E_l) \quad (14b)$$

Lorsque E_l est au voisinage immédiat du niveau de Fermi, le terme v_s^s est complètement négligeable devant le terme résonant de sorte qu'un développement de la solution de (11) en série par rapport à v_s^s est rapidement convergent.

Remarquons enfin que la transformation que nous avons faite est équivalente dans l'approximation de Hartree-Fock, à la transformation de Wolff-Schrieffer à partir de l'hamiltonien d'Anderson; il est aisé de montrer que, dans un alliage magnétique (14) entraîne l'existence d'une polarisation de spin identique à celle qui est obtenue dans la méthode de Wolff-Schrieffer.

(3) *Solution des équations de diffusion*

Nous résolvons le système (11) en remarquant que les équations sont découplées par paires (a,b), (c,d). Nous pouvons écrire la solution formelle de l'équation (11d) sous la forme:

$$G_{sq}^{dk} = \frac{1}{E^+ - E_{sq}} W_{sq}^d N^{-1} \sum_{k_0} G_{dk_0}^{dk} \quad (15a)$$

W_{sq}^d a été défini comme l'élément de matrice de l'opérateur $(1 - v_s^s G^{0s})^{-1} v_s^d$:

$$\langle sq | (1 - v_s^s G^{0s})^{-1} v_s^d | dk \rangle = W_{sq}^d. \quad (15b)$$

Remarquons que W_{sq}^d est indépendant de l'indice k ; les opérateurs V_j^i sont définis par:

$$V_j^i = P^j V P^i$$

où P^i est le projecteur complet sur les états i ($i = s, d$).

En notant:

$$G^{ds}(E) = N^{-1} \sum_k \frac{v_d^{sk} W_{sq}^d}{E^+ - E_{sk}} \quad (16)$$

l'équation (11c) devient:

$$G_{dq}^{dk} = \frac{1}{E^+ - E_{dq}} \left\{ \delta_{kq} + N^{-1} (v_d^d + G^{ds}) \times \sum_{k_0} G_{dk_0}^{dk} \right\}, \quad (17)$$

la solution de cette équation est immédiate et nous obtenons la solution de (11c, d) sous la forme:

$$G_{dq}^{dk} = \frac{1}{E - E_{dq}} \times \left\{ \delta_{kq} + N^{-1} \frac{v_d^d + G^{ds}}{1 - G^{0d}(v_d^d + G^{ds})} \frac{1}{E - E_{dk}} \right\} \\ G_{sq}^{dk} = \frac{N^{-1}}{E - E_{sq}} W_{sq}^d \frac{1}{1 - G^{0d}(v_d^d + G^{ds})} \frac{1}{E - E_{dk}}. \quad (18)$$

Nous résolvons de façon analogue les équations couplées (11a, b) et nous obtenons:

$$G_{sq}^{sk} = \frac{N^{-1} \langle sq | (1 - G^{0s} v_s^s)^{-1} | sk \rangle}{E - E_{sq}} \\ + \frac{N^{-2}}{E - E_{sq}} \frac{G^{0d}}{1 - G^{0d}(v_d^d + G^{ds})} \\ \times \sum_{k_1} \frac{\langle sq | (1 - G^{0s} v_s^s)^{-1} | sk_1 \rangle v_{sk_1}^d W_{sq}^{sk}}{(E - E_{sk_1})(E - E_{sk})}. \quad (19)$$

(4) *Charge déplacée, variation de densité d'états*

Nous évaluons la charge déplacée et la variation de densité d'états selon la méthode classique (cf. [1]); nous ne répétons pas ici le détail du raisonnement et nous nous contentons de donner le résultat.

De façon générale, la charge déplacée par l'impureté pour les énergies $E' < E$ comporte deux contributions:

$$Z(E) = Z^s(E) + Z^{dsd}(E). \quad (20)$$

$Z^s(E)$ est la charge déplacée par la bande 's' supposée seule

$$Z^s = \frac{1}{\pi} \text{Tr Im Log } (1 - v_s^s G^{0s}(E')) \quad (21)$$

$Z^{dsd}(E)$ est définie par:

$$Z^{dsd}(E) = \frac{1}{\pi} \text{Im Log } (1 - G^{0d}(E) \times (v_d^d + G^{ds}(E))) \quad (22)$$

où

$$G^{ds}(E) = N^{-2} \sum_{k, k'} v_d^{sk} \times [G^{0s}(1 - v_s^s G^{0s})^{-1}]_{k'k} v_s^{d k'},$$

est identique à la charge $Z^{ds} + Z^d$ trouvée pour une autre méthode dans la Réf. [1].

A l'ordre zéro par rapport à v_s^s , $Z^s = 0$ et nous obtenons:

$$Z^0(E) = Z^{0dsd}(E) = \pi^{-1} \text{Arg } (1 - G^{0d}(E) \times (v_d^d + G^{0ds})) \\ G^{0ds}(E) = N^{-1} \sum_{sk} \frac{|v_{sk}^d|^2}{E^+ - E_{sk}}. \quad (23)$$

Nous pouvons relier ce résultat [1] à celui d'Anderson [6]: si on développe au voisinage du pôle E_l de $v_{sk}^{(e)sk}$ (cf. (14)) l'équation (23), nous obtenons:

$$Z^0(E) = \pi^{-1} \text{Arg} \left\{ (E_l - E) \frac{d}{dE} \text{Log } G^{0d} \right\}_{E_l} \\ - G^{0d}(E) G^{0ds}(E) \}. \quad (24)$$

Si l'énergie E_i se trouve loin de la bande 'd', $G^{od}(E)$ varie comme E^{-1} et nous retrouvons l'expression d'Anderson[1].

Au premier ordre par rapport à v_s^s , nous obtenons, pour $Z^{ss}(E)$, le terme classique obtenu dans le modèle de bandes rigides:

$$Z^{ss}(E) = -\pi^{-1} \text{Im} N^{-1} \sum_{\mathbf{k}} \frac{v_{s\mathbf{k}}^{sk}}{E^+ - E_{s\mathbf{k}}} \\ = \frac{\Omega}{(2\pi)^3} \int_{S_s(E)} \frac{dS}{|\nabla_{\mathbf{k}} E_s|} v_{s\mathbf{k}}^{sk}. \quad (25)$$

(Ω est le volume atomique et $S_s(E)$ est la surface d'énergie constante $E = E_{s\mathbf{k}}$).

Le terme $Z^{dsd}(E)$ prend la forme suivante:

$$Z^{dsd}(E) = \pi^{-1} \text{Arg} \{ 1 - G^{od}(E) \\ \times (v_d^d + G^{ids}(E)) \} \\ G^{ids}(E) = G^{ods}(E) + N^{-2} \sum_{\mathbf{k}_0, \mathbf{k}_1} \frac{v_d^{sk_0}}{E - E_{s\mathbf{k}_0}} \\ \times \frac{v_{s\mathbf{k}_0}^{sk_1}}{E - E_{s\mathbf{k}_1}} \quad (26)$$

la variation de densité d'états $\delta n(E)$ introduite par l'impureté s'obtient à partir de (25) et (26) en appliquant la formule[7]:

$$\delta n(E) = \frac{1}{\pi} \frac{dZ}{dE}(E). \quad (27)$$

Rappelons enfin, que nous pouvons trouver l'expression de la matrice de transition $T(E)$ à partir de la connaissance des fonctions de Green[18, 19]. Nous pouvons ainsi obtenir les propriétés se rattachant à celle-ci (charge à grande distance, résistivité résiduelle etc. [8, 9]).

2. STRUCTURE ELECTRONIQUE DES ALLIAGES CuNi

Nous nous proposons de calculer, dans le modèle précédent, la charge déplacée, la

variation de densité d'états et la résistivité résiduelle des alliages CuNi. Nous présentons les hypothèses du calcul (Section 2(1)) avant de discuter les résultats obtenus pour $v_d^s, v_{s\mathbf{k}}^{sk}$ (Section 2(2)) pour la variation de densité d'états et la résistivité résiduelle (Section 2(3 and 4)).

(1) Structure de bandes du métal pur et hypothèses du calcul

Nous avons adopté pour la structure de bandes du cuivre un modèle analogue aux schémas d'interpolation proposés par de nombreux auteurs[10-12]. Nous prendrons comme point de départ le calcul de la densité d'état fait par Burdick[13] (du type APW) et nous ferons les hypothèses simplificatrices suivantes:

(a) *Bandes 'd'*. Les bandes 'd' auront une densité d'états $n(E)$ déduites des calculs de Burdick. Nous négligeons cependant la différence entre les densités d'états associées aux différentes orbitales 'd'; ceci permet de considérer les cinq bandes 'd' comme indépendantes et ayant chacune pour densité $n(E)/5$. La forme détaillée de la bande 'd' n'aura pas d'importance; seule la position du sommet de bande E_i par rapport à l'énergie de Fermi aura de l'importance: celle-ci $E_F - E_i$ 1.7eV est en accord avec les mesures optiques sur le cuivre.

(b) *Fonctions atomiques 'd'*. Nous n'avons pas calculé les fonctions atomiques 'équivalentes' donnant naissance à la structure de bandes 'd' du cuivre. Nous nous sommes contentés d'utiliser, soit des fonctions de Slater ($\Phi_{nl}(r) \approx r^l \exp -Zr$ [14]), soit des fonctions du type Watson[15] (combinaisons linéaires de fonctions de Slater). L'extension des fonctions 'd' aura une certaine importance (Section 2(2)) sur la forme de $v_{s\mathbf{k}}^d$ et donc sur la largeur de l'état lié virtuel.

(c) *Fonctions d'onde 's'*. Nous représentons les électrons 's' par une seule onde plane orthogonalisée aux couches internes et aux couches 'd'. Cette approximation est valable dans la mesure où nous ne nous intéressons

qu'aux énergies pour lesquelles le mélange des OPW n'est pas important (énergies voisines du bas de bande). C'est une approximation raisonnable *en moyenne* pour les états d'énergie de l'ordre de l'énergie de Fermi.

(d) *Relations de dispersion 's'*. Pour le calcul des éléments de matrice du potentiel d'impureté intervenant dans $v_s^* G^{1d*} \dots$, nous prendrons une relation de dispersion parabolique:

$$E_{\mathbf{k}} = E_0 + k^2/2m^* \quad (27)$$

cohérente avec l'hypothèse sur les fonctions d'onde. Nous négligeons donc les bandes d'énergies interdites introduites par le potentiel de réseau. Notons cependant que nous tenons compte de tous les états de conduction en supposant que la relation (27) est valable quel que soit $\mathbf{k}$. Les paramètres E_0 et m^* sont déterminés après ajustement au calcul de Burdick. ($E_0 - E_f = 7.54$ eV). Remarquons enfin que nous avons négligé (dans les équations 11) les effets de l'hybridation $s-d$ due à la matrice; nous tenons compte cependant en partie de celle-ci en prenant des bandes 'd' d'après un calcul APW.

(2) *Choix du potentiel d'impureté. Discussion des résultats du calcul de $v_{dm}^{\mathbf{k}}$*

En principe, nous devons déterminer le potentiel d'impureté à l'aide de la méthode de Hartree-Fock. Cependant, le problème d'autocohérence n'a pas été examiné dans le détail; la présente étude n'étant que préliminaire, nous n'avons assuré l'autocohérence que partiellement. Nous avons cherché le potentiel d'impureté parmi les potentiels du Yukawa du type:

$$V(r) = Q \frac{e^{-\gamma r}}{r} \quad (28)$$

où Q est la différence de valence entre l'impureté et la matrice. Le paramètre γ a été déterminé de façon autocohérente afin de satisfaire la règle de Friedel $Z = Z(E_F)$.

Le principal avantage des potentiels du type (28) est de permettre des calculs analytiques assez simples. Ce choix est justifié qualitativement de la façon suivante: (1) le potentiel peut être obtenu à l'aide de la méthode de Thomas Fermi linéarisée; celle-ci est valable dans la mesure où la perturbation est à variation spatiale relativement lente; (28) représente correctement le potentiel dans la région où les fonctions d'onde d sont importantes. (2) Nous pouvons obtenir une approximation du potentiel $V(r)$ en supposant que la répartition électrique dans l'alliage est la superposition des distributions électroniques des atomes de cuivre et de nickel. Le potentiel perturbateur est alors la simple différence des potentiels atomiques du nickel et du cuivre [16].

$$V(r) = V_{\text{Ni}}(r) - V_{\text{Cu}}(r).$$

Les configurations 's' étant supposées identiques pour le nickel et le cuivre, ce potentiel a effectivement un comportement analogue à celui du potentiel self consistant du type (28), les déviations par rapport à ce comportement n'étant importantes que dans la région où la densité électronique 'd' n'est pas importante. Un potentiel de ce type n'est qu'une approximation d'ordre zéro, la densité électronique 's' pouvant être modifiée par l'impureté. Nous verrons dans le cas du CuNi que cette modification est loin d'être négligeable. Ultérieurement, nous pensons obtenir une meilleure approximation en choisissant un potentiel de ce type où $V_{\text{Ni}}(r)$ est un mélange de configurations du nickel déterminé de façon autocohérente.

Dans la suite, nous utiliserons uniquement des potentiels de ce type; nous ne disposons donc d'aucun paramètre pour déterminer la structure électronique de l'impureté puisque γ sera obtenu par la règle de Friedel.

Nous avons effectué trois calculs différents désignés par: (a) calcul à l'ordre zéro par rapport à v_s^* avec des fonctions de Slater pour les fonctions $3d$ du cuivre. (b) calcul

au premier ordre par rapport à v^{ss} avec les fonctions $3d$ du type Slater et les fonctions internes calculées d'après [15]. (c) calcul au premier ordre par rapport à v^{ss} avec des fonctions internes et $3d$ du type Watson.

Nous caractérisons les résultats du calcul autocohérent par l'allure de:

$$v_{ik}^{dm} = Y_2^m(k) v^{ds}(k).$$

Nous donnons la partie radiale de cet élément de matrice dans la Fig. 1. Ce résultat s'explique par le fait que v_{ik}^{dm} est la somme de deux termes de signes opposés: le premier correspond à la partie d'électrons libres de la fonction 's', le second correspond à la partie d'orthogonalisation aux couches internes. Pour des petites valeurs de k , la partie d'orthogonalisation

l'emporte (v_k^d varie comme $|k|^2$). $v_k^{ds}(k)$ présente un maximum pour $k \approx k_M$ ($k_M \approx 1$ u.a.⁻¹ et $v_{ik}^{ds} \approx 2$ eV); la grandeur et la position de ce maximum sont relativement sensibles au choix de la fonction d'onde 'd' et du potentiel autocohérent correspondant (cf. Fig. 1). Pour de plus grandes valeurs de k ($k > k_M$), v_{ik}^d décroît et la partie d'électrons libres l'emporte; v^d change de signe pour $|k| \approx 2$ à 5 u.a., selon le type de calcul. Plus la portée du potentiel est petite, plus la courbe $v_{ik}^{ds}(k)$ est étalée.

Notons que la courbe obtenue présente une très grande analogie avec les coefficients d'hybridation H_{ik}^{skm} des fonctions s et d des métaux nobles intervenant dans les modèles d'interpolation tels que ceux de Mueller [10]. Par rapport au maximum de $H^{skm}(k)$, celui de

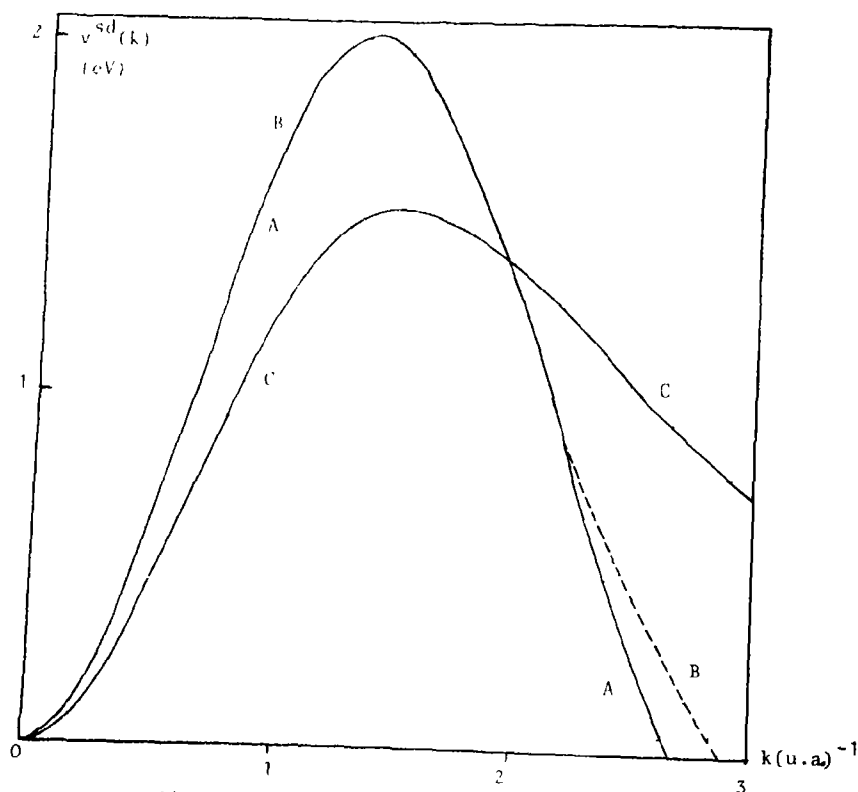


Fig. 1. Éléments de matrice $v_{ik}^{ds}(k)$ dans les cas d'étude A, B, C.

$v^{ad}(k)$ est déplacé vers les valeurs plus grandes du vecteur k et, de façon générale, $v^{ad}(k)$ est inférieur d'un facteur 2 à $H^{ad}(k)$.

(3) *Discussion des résultats du calcul de variation de densité d'états*

Nous obtenons un état lié virtuel quel que soit le type de calcul effectué ((a), (b) ou (c), cf. Section 2(2)). La variation de densité d'états est lorentzienne à mieux de 1 pour cent. En négligeant v_s^* , la largeur de l'état lié virtuel est alors donnée par l'expression classique [6]:

$$\Delta(E) = \text{Im} G^{0ds}(E) = \pi \langle |v_{\mathbf{k}}^d|^2 \rangle_E n_v(E). \quad (28)$$

où $\langle \rangle_E$ désigne la valeur moyenne sur la surface d'énergie constante $E = E_{\mathbf{k}}$.

Cependant, nous devons noter que l'approximation lorentzienne est d'autant plus valable que les largeurs de raie sont très faibles et de l'ordre du dixième d'électron volt. A cet égard, la dépendance angulaire de l'élément de matrice est importante puisque la valeur moyenne de $\langle |v_{\mathbf{k}}^d|^2 \rangle$ dont dépend $\Delta(E)$ (cf. (28)) est bien inférieure à la valeur de sa partie radiale $|v^{ds}(k)|^2 (v^{ds}(k_F) \approx 2\text{eV})$.

Les largeurs obtenues sont assez sensibles au choix de la fonction atomique de départ: si l'allure générale de $v^{ds}(k)$ n'est pas modifiée globalement par ce changement, la largeur variant comme $|v^{ds}(k)|^2$ peut être modifiée par un facteur deux.

Le potentiel v_s^* ne modifie pratiquement pas la forme de l'état lié virtuel; en effet, la modification de G^{ds} par v_s^* est très petite

$$\left| \frac{G^{1ds}(E) - G^{0ds}(E)}{G^{0ds}(E)} \right| \sim \frac{1}{20}$$

et le terme $Z^{dsd}(E)$ est donné pratiquement par son expression calculée pour $v_s^* = 0$.

Cependant, le terme v_s^* a une grande importance quantitative; bien qu'il ne fournisse qu'une variation de densité d'états $\delta n^s(E) (\ll \delta n^{dsd}(E))$ très faible, il contribue

de façon non négligeable à la charge d'écran par l'intermédiaire du terme de bandes rigides Z^{1s} . Dans le cas de l'alliage CuNi, v_s^* déplace 20 pour cent de la charge totale (calcul B, Tableau 1). De ce fait, la position du niveau résonant se déplace par rapport à celle qui est obtenue pour $v_s^* = 0$.

En conclusion, le terme v_s^* ne modifie pas la forme de l'état lié virtuel mais, en modifie la position par rapport au niveau de Fermi.

(4) *Comparaison avec les résultats expérimentaux*

Nous pouvons tenter de comparer les résultats de notre calcul avec les résultats obtenus expérimentalement.

Pour la résistivité résiduelle ρ , nous avons utilisé le fait que deux déphasages ('s' et 'd') étaient importants de sorte que, d'après [1]:

$$\rho = \frac{4\pi}{\alpha k_F} (\sin^2 \delta'_0 + 5 \sin^2 \delta'_2) \\ \delta'_0 = -\pi Z^s(E_F) \quad \delta'_2 = -\pi Z^{dsd}(E_F). \quad (29)$$

Les valeurs obtenues sont en bon accord avec l'expérience ($\rho_{\text{exp}} \approx 2\mu\Omega \text{ cm/pour cent}$).

Pour la variation de chaleur spécifique électronique, nous obtenons une valeur:

$$\Delta\gamma = \frac{2\pi}{3} k_B^2 \frac{d\delta'_2}{dE}(E_F) \quad (30)$$

bien supérieure à la valeur expérimentale [2]:

$$\frac{\Delta\gamma_{\text{th}}}{\Delta\gamma_{\text{exp}}} \sim 2.4$$

ceci confirme le fait que les états liés virtuels obtenus sont beaucoup trop étroits, d'autant plus que les valeurs expérimentales sont amplifiées par un coefficient d'augmentation par échange non négligeable.

Notons enfin que notre calcul souligne le fait que, dans l'interprétation des résultats expérimentaux, il est essentiel de tenir compte

Tableau I

$\nu(\text{u a}^{-1})$	ϵ_f^0	E	2Δ	$G_{\epsilon_f^0}^{00}$	$10 \beta \bar{\epsilon}_f^0$	$Z_{\epsilon_f^0}$	$Z_{\epsilon_f^0}^{00}$	$\Delta n_{\epsilon_f^0}$	$\Delta n_{\epsilon_f^0}^{00}$	$\Delta n_{\epsilon_f^0}^{00}$	$\frac{\Delta n_{\epsilon_f^0}^{00}}{\Delta n_{\epsilon_f^0}}$
A	2.106	3.117	7.437	0.0762	-0.143	0.0	0.0	0.100	0.0	0.815	7.94
					0.0136	0.0					
B	2.135	3.044	7.357	0.0664	-0.158	0.27	0.209	0.058	-0.0206	0.280	2.75
					0.0122	-0.030					
C	5.370	3.142	7.475	0.0375	-0.126	0.044	0.095	0.080	-0.0084	1.025	10.23
					0.0065	-0.004					

Nous avons défini β comme $G_{\epsilon_f^0}^{10}/G_{\epsilon_f^0}^{00}$. L'unité d'énergie est l'électron volt.
 Les quantités complexes $G_{\epsilon_f^0}^{00}$, β^* sont représentées par $(Re, -Im/\pi)$.

des déphasages 's' provenant de v_s^* . Une estimation de la largeur des états liés virtuels à partir de données expérimentales est délicate dans les alliages CuNi, CuCo puisque, non seulement les interactions électron-électron peuvent fausser les résultats, mais encore la diffusion s-s peut jouer un rôle non négligeable. Ainsi, sur la figure 2, nous avons reporté la largeur déduite de l'expérience en fonction de la fraction de résistivité $\xi = \rho(1=2)/\rho$ provenant de l'état lié virtuel.

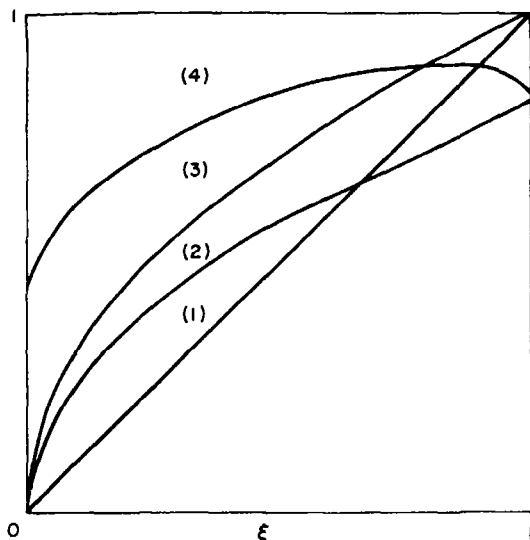


Fig. 2. Interprétation de la résistivité et de la chaleur spécifique du CuNi, à l'aide des déphasages δ_0 , δ_2 , en fonction du rapport ξ de la résistivité 'd' à la résistivité totale. $\Delta_0 = 0.182$ eV; $(E_F - E_{i0}) = 0.697$ eV; (1) Δ/Δ_0 ; (2) $10\delta_2(E_F)/\pi$; (3) $(E_F - E_1)/(E_F - E_{i0})$; (4) $Z(E_F) = (1/\pi)\{10\delta_2(E_F) + 2\delta_0(E_F)\}$.

3. CONCLUSION

Nous avons présenté les résultats d'un calcul préliminaire de la structure électronique des alliages CuNi. Nous avons utilisé un grand nombre d'hypothèses simplificatrices afin d'alléger le calcul numérique. Nous avons choisi pour la matrice une structure de bandes simplifiée analogue aux schémas d'interpolation établis pour les métaux nobles et de transition. Dans les limites de validité du modèle, nous avons montré l'existence d'un

état lié virtuel. La structure de celui-ci est assez sensible à la partie des fonctions d'ordre 3d ainsi qu'à celle du potentiel. La variation de densité d'états introduite par l'impureté est lorentzienne. La partie s du potentiel (v_s^*) n'intervient pas dans la largeur de la raie de résonance; elle peut intervenir dans la position de l'état lié virtuel parce que la charge déplacée par celle-ci n'est pas négligeable; de plus, la résistivité électrique peut être modifiée de façon importante par les termes v_s^* .

Cependant, les largeurs obtenues sont trop faibles pour rendre compte de l'ensemble des propriétés expérimentales. Nous pensons que les approximations que nous avons faites sur la structure de bandes ne modifient qualitativement le résultat sur l'ordre de grandeur des largeurs que dans la mesure où nous avons négligé l'hybridation s-d dans la matrice. Dans un article ultérieur, nous nous proposons de tenir compte simultanément de l'hybridation s-d de la matrice et de celle qui est due à l'impureté.

REFERENCES

1. RIEDINGER R. et GAUTIER F., *J. Phys. Chem. Solids* **31**, 2099 (1970).
2. GUTHRIE G. I. et al., *Phys. Rev.* **113**, 45, 793 (1959). DOMÉNICALI C. A. et CHRISTENSON E. I., *J. appl. Phys.* **34**, (1963).
3. FRIEDEL J., *Nuovo Cim. Suppl.* **7**, 287 (1958).
4. SLATER J. C. et KOSTER G. F., *Phys. Rev.* **95**, 1167 (1954).
5. DEMANGEAT Cl., *Thèse de 3e cycle*, Strasbourg (1969).
6. ANDERSON P. W., *Phys. Rev.* **124**, 41 (1961).
7. IFFSCHITZ E., *Adv. Phys.* **13**, 483 (1963).
8. BLANDIN A., *Thèse*, Paris (1961).
9. RIEDINGER R., *Thèse de 3e cycle*, Strasbourg (1969).
10. MUELLER F. M., *Phys. Rev.* **159**, 659 (1967).
11. JACOBS R. L., *J. phys. Soc.* **C492**, 1296, 1307 (1968).
12. HODGES L. I., EHRENREICH H. et LANG N. D., *Phys. Rev.* **152**, 505 (1966).
13. BURDICK G., *Phys. Rev.* **129**, 168 (1963).
14. SLATER J. C., *Phys. Rev.* **36**, 57 (1930).
15. WATSON R. E., *Phys. Rev.* **119**, 1934 (1960).
16. HERMANN N. F. et SKILLMANN S., *Atomic Structure Calculations*, Prentice Hall, New Jersey.
17. GOMES A. A., *J. Phys. Chem. Solids* **27**, 451 (1966). CAMPBELL I. A. et GOMES A. A., *Prog. phys. Sci.* **2-1** 1312 (1968).

ETUDE DE L'HYBRIDATION ENTRE BANDES s ET d DUE AU POTENTIEL D'IMPURETE DANS LES ALLIAGES DILUES A BASE DE METAUX NOBLES OU DE TRANSITION

R. RIEDINGER and F. GAUTIER

Laboratoire de Physique des Solides, Institut de Physique, 3, Rue de l'Université, Strasbourg, France

(Received 7 October 1969)

Résumé— Nous résolvons formellement le problème de l'hybridation introduite par une impureté entre les bandes s et d d'un métal noble ou de transition. Nous supposons les bandes s et d non hybridées dans le métal pur et nous représentons les bandes d en liaisons fortes. Nous appliquons ces résultats à un modèle simple dans lequel les électrons de la bande s ont comme fonctions d'onde des ondes planes modulées par la fonction de bas de bande; nous étendons l'analyse classique en déphasages à l'étude des alliages à base de métaux nobles et de transition; nous discutons notamment la forme asymptotique de la variation de densité électronique et la résistivité résiduelle.

Abstract— We present a general study of the hybridization introduced by an impurity between s and d bands of transition metals. We study a simple model assuming that s electrons are well described by plane waves modulated by the wave function of the bottom of the band. We extend the classical phase shift analysis to the study of impurities in transition metals. We discuss various physical properties of transitional alloys (residual resistivity, electronic density . . .).

Nous présentons un modèle permettant l'étude des alliages à base de métaux nobles et de transition dans l'approximation de Hartree-Fock; nous discutons en particulier l'effet des termes de mélange s - d dus à l'impureté, ainsi que le rôle du potentiel direct s - s sur les propriétés physiques de ces alliages.

Ce problème a déjà été abordé dans un modèle dû à Gomes[12] à propos de l'étude de la résistivité de la chaleur spécifique et du pouvoir thermoélectrique des alliages à base de métaux de transition. Dans ce modèle, la bande s et les bandes d sont traitées dans l'approximation des liaisons fortes. Le potentiel dû à l'impureté, supposé localisé sur le site de l'impureté, est déterminé par les trois éléments de matrice v^{ss} , v^{dd} , v^{sd} du potentiel entre les fonctions s et d de l'impureté.

Ce modèle ne saurait être que très qualitatif. En effet, il décrit de façon très imparfaite les bandes de conduction des métaux nobles et de transition: les calculs de structure de bandes et les modèles d'interpolation développés par de nombreux auteurs montrent

que, si dans ces métaux, les bandes d sont bien représentées par une approximation de liaisons fortes, les bandes de conduction sont décrites par un modèle d'électrons presque libres. De plus l'approximation de liaisons fortes pour les bandes de conduction ne peut évidemment tenir bien compte de l'ensemble de ces états. La convergence de la transformée de Hilbert de la densité d'états exige d'ailleurs que la bande ait une largeur finie W . Enfin, le potentiel d'impureté ayant la symétrie ponctuelle du réseau, l'élément de matrice v^{sd} est strictement nul si les bandes sont construites à partir d'états atomiques de symétries différentes de sorte que v^{sd} ne peut acquérir une signification précise que dans un calcul plus élaboré. L'existence des paramètres phénoménologiques W , v^{sd} , v^{ss} empêche toute application quantitative de ce modèle à un alliage particulier.

Le modèle que nous proposons est une extension du modèle de Gomes tenant compte d'une structure des bandes de conduction réaliste et permettant un calcul quantitatif

de la structure électronique des impuretés. Pour l'étude générale des effets de l'hybridation (notées s). Nous étudierons en détail ferons donc aucune hypothèse *a priori* sur la nature de l'ensemble des bandes de conduction (notées s'). Nous étudierons en détail deux cas particuliers correspondant à deux modèles réalistes des bandes de conduction:

(1) les fonctions d'onde s sont des ondes planes modulées par les fonctions de bas de bande; (2) les fonctions d'onde s sont traitées dans l'approximation des ondes planes orthogonalisées[8]; nous calculerons en particulier la structure électronique de l'alliage Cu Ni.

Dans notre modèle comme dans les modèles d'Anderson et de Gomes, nous négligeons l'hybridation $s-d$ de la matrice pure. Cette approximation est sévère dans les métaux de transition pour lesquels le niveau de Fermi tombe dans une région où les bandes de la matrice sont fortement hybridées (cas du fer par exemple). Elle peut également intervenir dans les métaux nobles (ou dans les métaux de transition) pour modifier la largeur des états liés virtuels, lorsqu'ils existent. L'origine de cet effet, discutée pour la première fois par Kanamori[23] est facilement compréhensible.

L'hybridation $s-d$ introduit une densité d'états faible et lentement variable avec l'énergie, l'état lié d extrait des bandes d pleines, entre en résonance avec ces états. La largeur de l'état correspondant à cette résonance ' dd ' supposée seule a été estimée dans le cuivre, à partir des calculs de structure de bandes de Burdick[24, 25] (Δ_d 0.1 eV). Bien qu'elle semble insuffisante pour expliquer les largeurs observées, elle n'est pas négligeable. Cet effet d'élargissement étant d'autant plus grand que l'état lié virtuel est plus proche du sommet des bandes d , il est certainement important pour les états liés virtuels apparaissant dans les alliages du type Ni Cr ou Co Ru[26]. Un traitement plus complet faisant intervenir simultanément l'hybridation liée du métal pur et de l'impureté montre d'ailleurs que ces deux effets ne sont pas additifs.

Nous développons actuellement cette étude afin de calculer son influence sur les diverses propriétés physiques des alliages.

Dans la première partie de cet article, nous étudions de façon générale le problème de l'hybridation $s-d$ due à l'impureté; nous résoudreons (ou supposerons résolu) le problème préliminaire de la diffusion dans chacune des bandes s et d séparément; c'est là un problème dont les résultats sont bien connus[5-7]. A l'aide des fonctions d'onde obtenues, nous déterminons les solutions de l'hamiltonien total en ajoutant l'hybridation due au potentiel d'impureté; nous obtenons ainsi une solution générale du problème, où le processus de mélange est clairement mis en évidence.

Dans la seconde partie de cet article, nous faisons une application du modèle général au cas où les fonctions d'onde s sont des ondes planes modulées par la fonction de bas de bande; en accord avec cette hypothèse, nous supposons donc que l'énergie des électrons ' s ' varie paraboliquement avec le vecteur d'onde k ($E = E_0 + k^2/2m$). Une telle structure de bandes représente raisonnablement les propriétés physiques des métaux considérés; nous pouvons alors calculer aisément la charge totale déplacée, la variation de densité électronique, la polarisation de spin (si l'impureté considérée est magnétique) et la résistivité résiduelle dans un métal noble ou de transition. Ces quantités sont exprimées à l'aide des déphasages introduits par le potentiel dans chaque bande ainsi qu'à l'aide des déphasages de mélange $s-d$. Dans le cas des métaux nobles, les formules classiques déduites d'un modèle à une bande[5] pour des électrons libres peuvent s'étendre sans grande modification; en particulier, pour un potentiel localisé sur le site de l'impureté, seul le déphasage $l=2$ (pour les électrons s) et les déphasages de symétrie d [7, 12, 23], sont modifiés du fait de l'existence du mélange. Nous pouvons ainsi faire aisément le lien avec la théorie de Friedel sur les états liés virtuels [9, 10]. Dans le cas des métaux de transition, les formules à une bande décrivant les pro-

priétés physiques de l'alliage à l'aide des déphasages ne peuvent s'étendre simplement: ainsi, il n'existe plus de relation simple entre les déphasages apparaissant dans la résistivité, la chaleur spécifique ou la variation de densité électronique. Ceci provient de l'existence de deux voies (*s* et *d*) et de la non conservation du nombre de particules dans chacune des voies.

Pour alléger les notations, nous avons développé le formalisme dans un modèle où les cinq bandes *d* sont indépendantes et où les densités d'états par unité d'énergie de chaque orbitale *i*, $n(E, \Gamma_i)$ sont égales [1]. Cette simplification n'entraîne pas de modification importante de la structure électronique des impuretés [27]. Les résultats théoriques sont généraux, et nous avons rétabli les indices Γ_i dans les formules finales pour tenir compte de ce fait.

Le travail que nous présentons permet une description unique des alliages à base de métaux nobles ou de transition; il est susceptible de s'appliquer tant aux alliages où il existe des états liés virtuels *s-d* (Cu Ni, Ni Cr, Co Os ...) que dans le cas où seules existent des résonances *d-d* [7] (alliages à base de Pd, Fe etc...). C'est donc une généralisation des modèles d'Anderson [9] et de Wolff [10] tenant compte explicitement de la structure de bandes des métaux considérés. Il doit être complété par une étude d'effet de l'hybridation *s-d* de la matrice.

1. PROBLEME GENERAL DE L'HYBRIDATION *s-d* DES ALLIAGES A BASE DE METAUX NOBLES OU DE TRANSITION

Après avoir discuté la méthode générale (1.1), nous donnons les équations relatives aux fonctions d'onde (1.2), à la variation de densité d'états et à la charge déplacée (1.3).

1.1 Méthode générale

L'hamiltonien de la matrice contenant une impureté située à l'origine s'écrit:

$$H = H_0 + V \quad (1.1)$$

où H_0 est l'hamiltonien du métal pur; les fonctions propres correspondantes sont des ondes de Bloch $|nk\rangle$ d'énergie $E_n^0(\mathbf{k})$:

$$H_0|nk\rangle = E_n^0(\mathbf{k})|nk\rangle \quad (1.2)$$

l'indice *n* représente la bande considérée ($n = s; d_i, i = 1, 5$); les états $|nk\rangle$ sont orthogonaux:

$$\langle nk|mk'\rangle = \delta_{nm}\delta(\mathbf{k} - \mathbf{k}') \quad (1.2b)$$

le potentiel d'impureté *V* est dû à la charge électrostatique supplémentaire *Z* apportée par l'impureté ainsi qu'à l'écran dû aux électrons de conduction. Nous supposons dans la suite que ce potentiel est local et est le même pour tous les électrons de même spin. De plus, sauf indication contraire, nous supposons que l'alliage n'est pas magnétique.

Afin de résoudre le problème de l'hybridation *s-d*, nous décomposons le potentiel d'impureté sous la forme:

$$V = V^{ss} + V^{dd} + V^{sd} + V^{ds} \quad (1.3a)$$

avec

$$V^{ij} = P^i V P^j \quad (1.3b)$$

où P^s est le projecteur sur les états *s* et P^d le projecteur sur l'ensemble des cinq bandes '*d*'. Nous décomposons donc l'hamiltonien (1.1) en deux parties:

$$\begin{aligned} H &= H_1 + H_2 \\ H_1 &= H_0 + V^{ss} + V^{dd} \\ H_2 &= V^{sd} + V^{ds} \end{aligned} \quad (1.4)$$

Nous cherchons les fonctions d'onde de H_1 sous la forme de combinaisons linéaires d'ondes de Bloch:

$$|\Psi_{nk}^1\rangle = \sum_{\mathbf{k}'} A^n(\mathbf{k}, \mathbf{k}') |nk'\rangle. \quad (1.5)$$

En effet, les opérateurs V^{ss} et V^{dd} étant hermitiques et les sous-espaces *s* et *d* orthogonaux, les solutions $|\Psi_{nk}^1\rangle$ sont contenues dans

l'espace n . L'équation de Schrödinger s'écrit simplement:

$$(H_0 + V^{nn})|\Psi_{nk}^1\rangle = \epsilon_{nk}|\Psi_{nk}^1\rangle. \quad (1.6a)$$

Dans $|\Psi_{nk}^1\rangle$ et dans ϵ_{nk} , l'indice n représente, soit les bandes de conduction (notées s) soit l'une des cinq bandes d (notées di , $i = 1, 5$).

Le potentiel d'impureté étant localisé, nous pouvons faire correspondre à toute onde $|nk\rangle$ une onde $|\Psi_{nk}^1\rangle$ de même énergie $\epsilon_{nk} = E_{nk}^0$ (à l'ordre N^{-1} près, N étant le nombre d'atomes du cristal); nous choisirons celle-ci de sorte qu'elle satisfasse à la condition aux limites:

$$\lim_{r \rightarrow \infty} \langle r | \Psi_{nk}^1 \rangle = \langle r | nk \rangle. \quad (1.6b)$$

De même, nous pouvons faire correspondre à chaque fonction $|nk\rangle$ une fonction propre $|\Psi_{nk}\rangle$ de l'hamiltonien total H :

$$H|\Psi_{nk}\rangle = E_{nk}|\Psi_{nk}\rangle \quad (n = s, di) \quad (1.7)$$

satisfaisant à une condition du type (1.6b). La fonction d'onde sera exprimée dans la base des fonctions propres de H_1 :

$$|\Psi_{nk}\rangle = \sum_{m,q} a_{nk}^{mq} |\Psi_{mq}^1\rangle \quad (1.8)$$

Les coefficients a_{nk}^{mq} vérifient le système d'équations suivant:

$$(E - E_{nk}^0) (-\delta_{kk'}\delta_{nn'} + a_{nk}^{nk'}) = \sum_{p,q} \langle \Psi_{mk}^1 | V | \Psi_{pq}^1 \rangle a_{nk}^{pq}. \quad (1.9)$$

Puisque seul le potentiel H_2 introduit des transitions entre ondes $|\Psi^1\rangle$, la somme $\sum_p$ est étendue aux cinq bandes d ($p = di$, $i = 1, 5$) si $m = s$; elle est étendue sur les seuls états de conduction si m correspond à l'une des bandes d ($m = di$).

Les équations (1.9) sont des équations de Fredholm inhomogènes de noyau $\langle \Psi_{mk}^1 | V | \Psi_{pq}^1 \rangle$. Ce système d'équations intégrales se simplifie notablement lorsque les bandes 'd' sont

traitées en liaisons fortes; dans ce cas, en effet, nous allons montrer que le noyau $\langle \Psi_{mk}^1 | V | \Psi_{pq}^1 \rangle$ ($m \neq p$) peut se mettre sous la forme d'une somme de produits d'une fonction de $\mathbf{k}f_{\alpha}(\mathbf{k})$ et d'une fonction de $\mathbf{k}'(\sum_{\alpha} f_{\alpha}(\mathbf{k})g_{\alpha}(\mathbf{k}'))$ (cf. Section [1.2]); les équations sont alors immédiatement solubles.

Pour calculer $\langle \Psi_{mk}^1 | V | \Psi_{pq}^1 \rangle$, il nous faut préciser les hypothèses du calcul des liaisons fortes: — les fonctions d'onde du métal pur $|d\mathbf{k}\rangle$ et les fonctions de l'alliage correspondant à $V^{sd} = 0$, $|\Psi_{d\mathbf{k}}^1\rangle$ s'écrivent sous la forme d'une combinaison linéaire d'orbitales atomiques $|j\lambda\rangle$ où j caractérise le type de l'orbitale et λ le site sur lequel elle est centrée:

$$|d\mathbf{k}\rangle = N^{-1/2} \sum_{m\lambda} a_m^1(\mathbf{k}) e^{i\mathbf{k}\lambda} |m\lambda\rangle \quad (1.10a)$$

$$|\Psi_{d\mathbf{k}}^1\rangle = N^{-1/2} \sum_{m\lambda} A_{m\lambda}^{d\mathbf{k}} |m\lambda\rangle. \quad (1.10b)$$

Nous supposons dans la suite, pour fixer les idées, que le groupe ponctuel du cristal est cubique et nous choisirons les fonctions atomiques de sorte qu'elles soient fonctions de base des représentations irréductibles $\Gamma_{25}^-(m = 1, 2, 3)$ et $\Gamma_{12}^-(m = 4, 5)$.

En accord avec les calculs de liaisons fortes, nous supposons que les fonctions atomiques sont quasi orthogonales:

$$\langle m\lambda | n\mu \rangle = \delta_{mn}\delta_{\lambda\mu}. \quad (1.11)$$

Dans ces conditions, en introduisant le projecteur complet sur les états d :

$$P^d = \sum_{i,\lambda} |i\lambda\rangle \langle i\lambda| \quad (1.12)$$

dans l'élément de matrice du potentiel nous obtenons:

$$\langle \Psi_{mk}^1 | V | \Psi_{d\mathbf{k}}^1 \rangle = N^{-1} \sum_{m\lambda} v_{mk}^{dm\lambda} A_{m\lambda}^{d\mathbf{k}} \quad (1.13)$$

avec la notation:

$$v_{mk}^{dm\lambda} = N^{1/2} \langle \Psi_{mk}^1 | V | m\lambda \rangle. \quad (1.14)$$

Le noyau de l'équation (1.9) s'écrit donc

comme la somme de produits de fonctions de $\mathbf{k}$ et de fonctions de $\mathbf{k}'$; le potentiel d'impureté étant localisé au voisinage de l'impureté, les éléments de matrice (1.14) décroissent très rapidement avec la distance $|\lambda|$, de sorte qu'il suffira dans la pratique de ne prendre que les termes correspondant à l'impureté $\lambda = 0$ et (éventuellement) à ses premiers voisins [7].

Remarquons enfin que le développement du type (1.13) peut être étendue à une bande quelconque pourvu qu'on remplace les états atomiques $|i\lambda\rangle$ par les fonctions de Wannier correspondantes. Cependant, en général les fonctions de Wannier sont étendues même dans le cas de cinq bandes d hybridées et le développement précédent ne converge pas rapidement, ce qui lui enlève son utilité pratique.

1.2 Fonctions d'onde de l'alliage

Grâce à la forme (1.13) du noyau, nous pouvons résoudre facilement les équations (1.9). Désignant par $\alpha = (m, \lambda)$ l'ensemble des indices m et λ , nous définissons les deux matrices:

$$G_{1\alpha}^{d\alpha'} = N^{-1} \sum_{j,k} \frac{A_{\alpha}^{jk} A_{\alpha'}^{jk}}{E - E_{jk}^0} \quad (1.15a)$$

$$G_{1\alpha}^{ds\alpha'} = N^{-1} \sum_k \frac{v_{\alpha}^{sk} v_{\alpha'}^{sk}}{E^+ - E_{sk}^0}. \quad (1.15b)$$

Equation (1.15a) sont les éléments de matrice dd de l'opérateur de Green associé à H_1 , $G_1 = (E - H_1)^{-1}$. Selon l'habitude et pour fixer le comportement asymptotique de $\langle \mathbf{r} | n \mathbf{k} \rangle$, nous supposons que $E^+ = E + i0$. Dans la suite, nous omettrons l'exposant associé à E . En utilisant le fait que le noyau de (1.9) se met sous la forme (1.14), nous obtenons pour les fonctions d'onde les expressions suivantes:

$$a_{sk'}^{jk} = \delta_{kk'} + \frac{1}{N} \frac{1}{E - E_{ik'}^0} \sum_{\alpha, \beta} v_{\alpha}^{jk'} v_{\beta}^{sk} \times \{ (1 - G_1^d G_1^{ds})^{-1} G^d \}_{\alpha\beta} v_{\beta}^{sk}$$

$$\begin{aligned} a_{djk'}^{jk} &= \frac{1}{N} \frac{1}{E - E_{djk}^0} \sum_{\alpha, \beta} A_{\alpha}^{djk'} \times \{ (1 - G_1^{ds} G_1^d)^{-1} \}_{\alpha\beta} v_{\beta}^{jk} \\ a_{djk'}^{jk} &= \delta_{ij} \delta_{kk'} + \frac{1}{N} \frac{1}{E - E_{djk'}^0} \sum_{\alpha, \beta} A_{\alpha}^{djk'} \times \{ G_1^{ds} (1 - G_1^d G_1^{ds})^{-1} \}_{\alpha\beta} A_{\beta}^{djk} \\ a_{sk'}^{jk} &= \frac{1}{N} \frac{1}{E - E_{sk'}^0} \sum_{\alpha, \beta} v_{\alpha}^{sk'} v_{\beta}^{jk} \times \{ (1 - G_1^d G_1^{ds})^{-1} \}_{\alpha\beta} A_{\beta}^{djk}. \quad (1.16) \end{aligned}$$

Rappelons que, dans ces expressions $\alpha = (m\lambda)$, $m = s$ ou di . Ces expressions sont complexes; nous verrons cependant que la forme asymptotique de la fonction d'onde, qui intervient dans les problèmes de résistivité, de charge déplacée etc... prendra une forme simple (voir Section 2).

1.3 Charge totale déplacée; variation de densité d'états introduite par l'impureté

Nous déterminons la densité d'états et la charge déplacée par le potentiel V à l'aide de l'opérateur de Green $G = (E^+ - H)^{-1}$ selon le schéma utilisé par de nombreux auteurs [11-13]. La variation de densité d'états introduite par l'impureté est donnée par:

$$\delta n(E) = \text{Tr}(\delta(E - H) - \delta(E - H_0)). \quad (1.17)$$

Celle-ci est reliée à la fonction de Green G par les relations:

$$\begin{aligned} \text{Im Tr } G &= -\pi \text{Tr } \delta(E - H) \\ \text{Im Tr } G^0 &= -\pi \text{Tr } \delta(E - H_0). \end{aligned} \quad (1.18)$$

Nous nous intéressons ici uniquement à la variation de densité d'états due à l'hybridation de sorte que nous écrirons $\delta n(E)$ sous la forme:

$$\delta n(E) = \delta n^s(E) + \delta n^d(E) + \delta n^{sd}(E). \quad (1.19)$$

Dans (1.19), $\delta n^s(E)$ représente la variation de densité électronique introduite dans la bande s par V^{ss} ; de même $\delta n^d(E)$ représente la variation dans la bande d introduite par V^{dd} ; $\delta n^{sd}(E)$ est le terme dû au mélange $V^{sd} + V^{ds}$. D'après (1.18) et (1.17), ce terme s'écrit simplement:

$$\delta n^{sd}(E) = -\frac{1}{\pi} \text{Tr}(G - G_1). \quad (1.20)$$

L'opérateur G est donné en fonction de G_1 à l'aide de l'équation classique [14]:

$$G = G_1(V^{ds} + V^{sd})G + G_1. \quad (1.21)$$

Nous évaluerons la trace apparaissant dans (1.20) à l'aide des éléments de matrice de G et G_1 dans la représentation intermédiaire des fonctions $|\Psi_{nk}^i\rangle$. Les équations satisfaites par ces éléments de matrice sont analogues aux équations (1.9). Nous ne la reproduisons pas ici, le principe de résolution est le même que celui qui permet d'obtenir les fonctions d'onde de l'alliage. On montre alors aisément que (1.20) se met sous la forme suivante:

$$\delta n^{sd}(E) = \frac{1}{\pi} \frac{d}{dE} \text{Arg det}(1 - G_1^d G_1^{ds}). \quad (1.22)$$

La charge déplacée par l'impureté et due au mélange s'écrit alors:

$$\begin{aligned} Z^{sd}(E) &= \int_{-E}^E \delta n^{sd}(E') dE' \\ &= \frac{1}{\pi} \text{Arg det}(1 - G_1^d G_1^{ds}). \end{aligned} \quad (1.23)$$

Cette expression est valable quelles que soient les bandes s et d . Rappelons que les fonctions G_1^d et G_1^{ds} (définies par (1.15)) sont relatives à l'hamiltonien H_1 ; elles contiennent donc implicitement l'effet du potentiel $V^{ss} + V^{dd}$ et ne se ramènent pas directement aux fonctions de Green du métal pur.

La charge déplacée due au mélange se calcule donc à l'aide d'un déterminant de

rang $5n$ (n est le nombre de sites λ où $v_{\lambda\lambda}^{ss}$ est non négligeable). La résolution explicite peut être simplifiée par la théorie des groupes selon la même méthode que celle utilisée pour l'étude des perturbations à l'intérieur des bandes étroites [7]. Z^{sd} est alors la superposition de déphasages associés à chacune des représentations irréductibles du groupe ponctuel du cristal. En particulier, dans le cas où le potentiel est localisé sur l'impureté, la charge déplacée s'écrit sous la forme:

$$Z(E) = Z^s(E) + Z^d(E) + Z^{sd}(E) \quad (1.24a)$$

$$Z^{sd}(E) = \frac{2}{\pi} \{3\delta^{sd}(E, \Gamma'_{25}) + 2\delta^{sd}(E, \Gamma'_{12})\} \quad (1.24b)$$

avec

$$\delta^{sd}(E, \Gamma') = \text{Arg}(1 - G_{10}^{ds} G_1^{sd} G_{10}^{ds}). \quad (1.24c)$$

En effet, dans ce cas, le déterminant apparaissant dans (1.22) (1.23) a pour rang 5 et est directement diagonalisé dans la base des fonctions $|i0\rangle$ puisque G_1^d et G_1^{ds} sont transformées identiquement par les opérations du groupe ponctuel du cristal. Les formules (1.22) (1.23) généralisent les résultats obtenus à une bande. Elles introduisent des déphasages de mélange dont la signification physique est claire: le potentiel perturbateur ayant la symétrie cubique, on peut choisir comme fonctions propres de H_1 les fonctions se transformant comme les fonctions de base des représentations irréductibles du groupe cubique $|\Psi_n^i(\Gamma')\rangle$; le potentiel d'hybridation $V^{sd} + V^{ds}$ n'introduit d'interaction qu'entre les ondes $|\Psi^i\rangle$ qui se transforment de manière similaire par les opérateurs du groupe ponctuel; le déphasage $\delta^{sd}(\Gamma')$ traduit l'interaction entre ces ondes partielles.

Nous ne développons pas plus loin le formalisme général, bien qu'il puisse s'appliquer sans difficulté; nous allons étudier dans la deuxième partie de cet article un modèle simple de structure de bandes d'un métal de transition permettant un calcul analytique complet des propriétés physiques de l'alliage.

2. APPLICATION: GENERALISATION DE L'ANALYSE EN DÉPHASAGES AUX ALLIAGES A BASE DE MÉTAUX NOBLES ET DE TRANSITION

L'analyse en déphasages n'a été faite que dans le cas où la bande *s* peut être assimilée à une bande d'électrons libres dont les fonctions d'onde sont des ondes planes modulées par la fonction de bas de bande $u(\mathbf{r})$:

$$\langle \mathbf{r} | s \mathbf{k} \rangle = N^{-1/2} u(\mathbf{r}) e^{i \mathbf{k} \cdot \mathbf{r}}. \quad (2.1a)$$

Nous supposons que tel est le cas dans la suite de ce paragraphe. De plus, pour simplifier les développements, nous supposons que

(1) les cinq bandes *d* sont identiques et indépendantes, i.e.:

$$|d i \mathbf{k}\rangle = \frac{1}{\sqrt{N}} \sum_{\lambda} e^{i \mathbf{k} \cdot \lambda} |i \lambda\rangle, \quad n(E, \Gamma i) = \langle i 0 | \delta \times (E - H_0) | i 0 \rangle = n(E)/5. \quad (2.1b)$$

(2) le potentiel d'impureté est localisé sur l'impureté et a la symétrie sphérique.

Ces deux approximations sont raisonnables; elles sont justifiées par différents calculs de structure électronique d'alliages à base de métaux nobles et de transition. La première n'est introduite que pour simplifier l'exposé; nous donnerons d'ailleurs les formules finales en faisant réapparaître les densités d'états partielles $n(E, \Gamma_i)$. La seconde hypothèse simplifie les calculs pratiques; il est possible d'étendre l'analyse en traitant les potentiels au delà des premiers voisins par une méthode de perturbation; ceci complique considérablement les calculs et n'est pas essentiel sauf dans des cas pathologiques (Ni Cu, Pt Au) où le potentiel est nécessairement étendu [27].

Afin d'appliquer le formalisme précédent, nous rappelons d'abord les résultats d'un calcul de diffusion dans chacune des bandes *s* et *d* supposées indépendantes (détermination des fonctions $|\Psi_{nk}^i\rangle$) (Section 2.1); nous déterminons ensuite la charge déplacée, Section 2.2, les fonctions d'onde de l'alliage, ainsi

que leur forme asymptotique, Section 2.3; nous discutons la forme de l'amplitude de diffusion élastique en séparant le cas des alliages à base de métaux nobles et de transition. Les résultats sur l'amplitude de diffusion permettent de déterminer la résistivité électrique (2.4) et la forme asymptotique de la variation de densité électronique; nous insistons dans ces paragraphes sur la différence de comportement entre les deux types d'alliages considérés, en ce qui concerne la représentation physique à l'aide des déphasages. Enfin, nous discutons brièvement l'influence du potentiel de diffusion *s-s* sur la polarisation de spin introduite par une impureté magnétique dans un alliage à base de métal noble, en liaison avec les études récentes sur l'intégrale d'échange dans les alliages du type Cu Mn, Fe, Cr [21].

2.1 Diffusion dans les bandes *s* et *d*; fonctions $|\Psi_{nk}^i\rangle$

Grâce aux hypothèses faites sur les bandes *d*, l'élément de matrice $v^{dd} = \langle i 0 | V | i 0 \rangle$ détermine entièrement le potentiel d'impureté; d'après les résultats classiques sur la diffusion dans les bandes étroites, les fonctions $|\Psi_{nk}^i\rangle$ sont données par [6, 10]

$$\Psi_{dk}^i(\mathbf{r}) = N^{-1/2} \sum_{\lambda} A_{\lambda}^{dk} \phi^d(\mathbf{r} - \lambda) \quad (2.2a)$$

$$A_{\lambda}^{dk} = e^{i \mathbf{k} \cdot \lambda} + \frac{v^{dd}}{1 - v^{dd} G^{0d}} G^{0d}(\lambda). \quad (2.2b)$$

G^{0d} est défini comme l'élément de matrice de l'opérateur de Green du métal pur entre fonctions atomiques centrées sur le site de l'impureté:

$$\langle d i 0 | G^0 | d j 0 \rangle = G^{0d}(E, \Gamma_i) \delta_{ij} \quad (2.3)$$

$$\langle d i 0 | G^0 | d i \lambda \rangle = G_{i0}^{0d}(\lambda).$$

Dans le cas de cinq bandes indépendantes, ces fonctions sont indépendantes de *i*.

La fonction $G_{i0}^{d i 0}$ définie par (1.15) devient (en omettant les indices *i 0* pour simplifier):

$$G_1^d(E) = G_{10}^d = N^{-1} \sum_{\mathbf{k}} \frac{|A_{10}^{d\mathbf{k}}|^2}{E - E_{d\mathbf{k}}^0}. \quad (2.4)$$

En utilisant l'équation de Dyson appliquée à G_1^d :

$$G_1^d = G^0 + G^0 V^{dd} G_1^d$$

nous obtenons

$$G_1^d(E) = \langle i0 | G_1^d | i0 \rangle = \frac{G^{dd}(E)}{1 - V^{dd} G^{dd}(E)}. \quad (2.5)$$

D'après l'hypothèse faite sur la bande s du métal pur, les fonctions propres $|\mathbf{s}\mathbf{k}\rangle$ ont une énergie donnée par:

$$E_{\mathbf{s}\mathbf{k}}^0 = \frac{\hbar^2 k^2}{2m^*}; \quad (2.6)$$

d'après les résultats obtenus dans l'approximation de la masse effective et dans l'approximation sphérique ici utilisée [13, 15], les fonctions d'onde diffusées par $V(r)$ se mettent sous la forme:

$$\langle \mathbf{r} | \Psi_{\mathbf{s}\mathbf{k}}^d \rangle = N^{-1/2} u(r) f(\mathbf{r}) \quad (2.7)$$

où $f(\mathbf{r})$ est solution de l'équation de masse effective:

$$\left\{ \Delta/2m^* - E + V(r) \right\} f(r) = 0. \quad (2.8)$$

Nous résoudrons cette équation en coordonnées sphériques puisque le potentiel $V(r)$ est supposé avoir la symétrie centrale; la fonction $f(r)$ se met alors sous la forme,

$$f_l(r) Y_l^m(\hat{r}) \quad (2.9)$$

où $Y_l^m(\hat{r})$ est l'harmonique sphérique classique associée à la direction $\hat{r}$ [14] et où $f_l(r)$ satisfait à l'équation radiale:

$$\left\{ \frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} - 2m^* V(r) + k^2 \right\} r f_l(r) = 0, \quad (2.10)$$

Les fonctions $f_l(r)$ sont régulières à l'origine et sont normalisées selon la condition classique:

$$\lim_{r \rightarrow \infty} f_l(r) = \sin(kr - l\pi/2 + \delta_l(k)) \quad (2.11)$$

$\delta_l(k)$ est le déphasage introduit par la partie s du potentiel perturbateur. D'après les résultats classiques [14], la fonction d'onde s associée à la fonction de Bloch $|\mathbf{s}\mathbf{k}\rangle$ s'écrira:

$$\Psi_{\mathbf{s}\mathbf{k}}^d(\mathbf{r}) = N^{-1/2} u(r) \frac{4\pi}{kr} \sum_{l,m} i^l e^{i\delta_l} Y_l^m(\hat{r}) f_l(kr). \quad (2.12)$$

2.2 Potentiel perturbateur et charge déplacée

Nous appliquons dans ce paragraphe le résultat (1.24) en utilisant ceux du paragraphe précédent.

Grâce aux formules (2.2) et (2.12), nous pouvons déterminer les éléments de matrice du potentiel V^{sd} :

$$v_{m0}^{s\mathbf{k}} = - \frac{4\pi}{k} e^{-i\delta_2(k)} Y_2^m(\hat{k}) v^{sd}(k) \quad (2.13a)$$

$$v^{sd}(k) = 4\pi \int_0^\infty \phi^d(r^*) V(r) u(r) f_2(kr) r dr. \quad (2.13b)$$

Dans (2.13), $\phi^d(r)$ est la partie radiale de la fonction atomique d et $f_2(kr)$ est défini par (2.10), (2.11). Les formules (2.13) appellent les commentaires suivants:—le potentiel d'hybridation (2.13a) a la symétrie d par rapport à la direction de $\mathbf{k}$ —la partie radiale de ce potentiel ($v^{sd}(k)$) dépend de la partie s du potentiel par l'intermédiaire de la fonction $f_2(kr)$; elle ne dépend pas explicitement de la partie d , puisque dans l'approximation des liaisons fortes, la dépendance radiale de la fonction d'onde $\phi^d(r)$ n'est pas modifiée par V^{dd} .

Remarquons enfin que la fonction G_1^{ds} (cf. 1.15) s'écrit ici avec l'hypothèse des bandes indépendantes, sous la forme:

$$G_1^{ds} = G_1^{ds}(E) = \frac{\Omega}{(2\pi)^3} \int_0^\infty \frac{|\nu^{sd}(k)|^2}{E - k^2/(2m^*)} dk. \quad (2.14)$$

Dans cette formule, Ω est le volume atomique. En séparant parties réelles et imaginaires de G_1^{ds} , nous obtenons:

$$G_1^{ds} = f^{ds} - i\pi n^{ds} \quad (2.15a)$$

$$n^{ds} = \frac{m^* \Omega |\nu^{sd}(\sqrt{2m^*E})|^2}{(2\pi)^3 \sqrt{2m^*E}} \quad (2.15b)$$

$$f^{ds} = P \int \frac{n^{ds}(E')}{E - E'} dE'. \quad (2.15c)$$

Dans (2.15c), P est la partie principale au sens de Cauchy. Puisque nous avons supposé les cinq bandes d indépendantes et le potentiel d'impureté à symétrie sphérique, les cinq déphasages de mélange définis par (1.24) sont égaux dans le cas de bandes identiques:

$$\delta^{sd}(E, \Gamma) = \delta^{sd}(E) \\ = \text{Arctg} \frac{\text{Im} G_1^d(E) G_1^{ds}(E)}{1 - \text{Re} G_1^d(E) G_1^{ds}(E)}. \quad (2.16)$$

Les quantités G_1^d et G_1^{ds} sont données respectivement par (2.5) et (2.15).

La charge déplacée dans la bande s supposée seule est donnée par la règle de Friedel

$$Z^s(E) = \frac{2}{\pi} \sum_{l=0}^{\infty} (2l+1) \delta_l(E) \quad (2.17)$$

où les déphasages dans la bande s sont déterminés par (2.11). De même, la charge déplacée dans la bande d est donnée pour un potentiel localisé par la relation:

$$Z^d(E) = \frac{2}{\pi} (3\delta(\Gamma'_{25}, E) + 2\delta(\Gamma'_{12}, E)) \quad (2.18)$$

où les déphasages $\delta(\Gamma', E)$ sont égaux dans le cas de bandes identiques; ils sont donnés par la relation:

$$\text{tg} \delta(\Gamma, E) = - \frac{\pi n^d(E, \Gamma) v^{dd}}{1 - v^{dd} f(E, \Gamma)} \\ = \text{Arg} (1 - v^{dd} G^{dd}(\Gamma)) \quad (2.19)$$

où $f(E, \Gamma) = \text{Re} G^{dd}$ et $n(E, \Gamma) = -\pi^{-1} \text{Im} G^{dd} = n(E)/5$; $f(E, \Gamma)$ est la transformée de Hilbert de $n(E, \Gamma)$ (cf. 2.15c)

$$f(E, \Gamma) = P \int \frac{n(E', \Gamma)}{E - E'} dE'. \quad (2.20)$$

2.3 Discussion des formules donnant la charge déplacée: état lié virtuel

Dans le cas d'un métal de transition où la bande d est incomplète, les déphasages dans les deux bandes jouent *a priori* le même rôle; cependant, la charge déplacée dans la bande d étant plus importante que celle déplacée dans la bande s [7] nous pouvons dire que l'effet du mélange est de renormaliser les déphasages $\delta^d(E, \Gamma)$ en les remplaçant par $\delta^d + \delta^{sd}$ (cf. (1.24), (2.26), (2.19)).

Dans le cas d'un métal noble, où la bande d est complète, les déphasages d au voisinage du niveau de Fermi sont nuls (modulo π) puisque $n^d(E)$ est nul (cf. 2.19). Il n'y a pas d'ambiguïté: l'effet du mélange est de remplacer le déphasage $l = 2$ introduit dans la bande s par un déphasage:

$$\delta'(E, \Gamma) = \delta_2(E) + \delta^{sd}(E, \Gamma).$$

Nous pouvons alors retrouver clairement l'origine d'un état lié virtuel $s-d$ dans les métaux nobles ou de transition. Lorsque le potentiel d'impureté V est suffisamment répulsif, il extrait un état d de la bande d pleine; l'énergie de celui-ci E_l^0 est donnée (en l'absence d'hybridation) par le pôle de (2.19):

$$1 - v^{dd} R(E_l^0) = 0.$$

Au voisinage de cette énergie, le déphasage $\delta_2(E)$ reste régulier, tandis que le déphasage de mélange saute de $-\pi$ à 0 lorsque l'énergie passe de valeurs inférieures à des valeurs sup-

érieures à E_f^0 . En effet, d'après (2.16) et en utilisant le fait que la densité d'états est nulle pour les énergies considérées, $\delta^{sd}(E)$ s'écrit sous la forme:

$$i g \delta^{sd}(E, \Gamma) = - \frac{\pi n^{ds}(E, \Gamma) f(E, \Gamma)}{1 - f(E, \Gamma) (v^{dd} + f^{ds}(E, \Gamma))}. \quad (2.21)$$

La position de la résonance E_f^0 , donnée par le zéro du dénominateur de (2.11),

$$1 - f(E, \Gamma) (v^{dd} + f^{ds}(E, \Gamma)), \quad (2.22)$$

est déplacée par le mélange s - d . La largeur de l'état lié virtuel est donnée par le développement de (2.11) au voisinage du dénominateur.

$$i g \delta^{sd}(E, \Gamma) = \frac{\Delta(E, \Gamma)}{E - E_f^0} \quad (2.23a)$$

$$\Delta(E, \Gamma) = \pi n^{ds} f(E, \Gamma) / f'(E, \Gamma) \quad (2.23b)$$

les formules (2.22), (2.23) généralisent la formule d'Anderson en tenant compte explicitement de la structure de bandes d sur celle de l'état lié virtuel. Nous pouvons d'ailleurs retrouver les formules d'Anderson[9] en supposant que le potentiel v^{dd} est suffisamment grand pour que l'on puisse assimiler, au voisinage de E_f^0 , $f(E, \Gamma)$ à sa forme asymptotique (cf. (2.15c))

$$\lim_{E \rightarrow E_f^0} f(E, \Gamma) = E^{-1}. \quad (2.23c)$$

Dans ces conditions, (2.23) devient

$$\Delta(E, \Gamma) = \pi n^{ds}(E, \Gamma) = \pi \langle |v^{sd}(\mathbf{k})|^2 \rangle_f n^s(E); \quad (2.23d)$$

dans (2.23c), $\langle \rangle_f$ désigne la valeur moyenne de $|v^{sd}(\mathbf{k})|^2$ sur la surface d'énergie constante E . L'étude du comportement de f^{ds} montre qu'un tel développement est valable pour l'énergie de Fermi des métaux nobles[8], la distance entre le sommet des bandes d et le niveau de Fermi étant assez grande ($\sim$ eV).

Il n'en est probablement plus de même pour les états liés virtuels apparaissant dans les métaux ferromagnétiques (NiCr, NiRu par exemple); dans ce cas, il semble qu'il faille tenir compte de la proximité de la bande d , cet effet ayant une importance pour des énergies de l'ordre de la largeur de l'état lié virtuel[16].

Notons enfin que la forme de la résonance n'est pas affectée par les termes v^{ss} dans la mesure où le déphasage $\delta_s(E)$ a un comportement régulier dans le domaine d'énergie $(E_f^0 - \Delta, E_f^0 + \Delta)$.

2.4 Fonctions d'onde de l'alliage

Grâce au résultat (1.16) et aux formules (2.2) et (2.12) relatives à $\Psi_{nk}^l(\mathbf{r})$, on obtient complètement les fonctions de l'alliage. La fonction $|\Psi_{nk}\rangle$ associée à la fonction de Bloch $|\mu\mathbf{k}\rangle$ s'écrit sous la forme:

$$\Psi_{nk}(\mathbf{r}) = \Psi_{nk}^l(\mathbf{r}) + \sum_m \Psi_{nk}^m u(\mathbf{r}) \quad (2.24)$$

$|\Psi_{nk}^m\rangle$ représente la fonction d'onde diffusée dans la bande m par le potentiel de mélange $v^{sd} + v^{ds}$. Nous obtenons:

$$\Psi_{nk}^{s, ds}(\mathbf{r}) = -N^{-1/2} \frac{5}{kr} e^{i\delta_s(k)} P_2(\cos \theta) v^{sd}(k)$$

$$\times \frac{G_1^d}{1 - G_1^d G_1^{ds}} u(r) J_s(E, r)$$

$$\Psi_{nk}^{d, dd}(\mathbf{r}) = -N^{-1/2} \frac{1}{1 - G_1^d G_1^{ds}} \frac{4}{kr}$$

$$\times v^{sd}(k) e^{i\delta_s(k)} Y_2^m(\hat{k})$$

$$\sum_{\lambda} \phi_m(\mathbf{r} - \boldsymbol{\lambda}) J_{dm}(E, \boldsymbol{\lambda})$$

$$\Psi_{dmk}^{d, ds}(\mathbf{r}) = \delta_{mm'} \frac{1}{\sqrt{N}} \frac{A_{m0}^{dk} G_1^{ds}}{1 - G_1^d G_1^{ds}} \times \sum_{\lambda} \phi_m(\mathbf{r} - \boldsymbol{\lambda}) J_{dm}(E, \boldsymbol{\lambda}) \quad (2.25)$$

$$\Psi_{dmk}^{s, ds}(\mathbf{r}) = N^{-1/2} 4 \frac{A_{m0}^{dk}}{1 - G_1^d G_1^{ds}}$$

$$\times Y_2^m(\hat{r}) \frac{u(r)}{r} J_s(E, r).$$

Dans ces expressions, nous avons défini les quantités J_s et J_d par les relations:

$$J_s(E, \mathbf{r}) = \frac{\Omega}{(2\pi)^3} \int_0^\infty \frac{f_2(k'r) \nu^{sd}(k')}{E - E_{sk'}^0} dk' \quad (2.26a)$$

$$J_{dm}(E, \lambda) = \frac{1}{N} \sum_k \frac{A_{m0}^{dk} A_{m\lambda}^{dk*}}{E - E_{dmk}^0} = \frac{G^{0d}(\lambda)}{1 - v^{dd} G^{0d}}. \quad (2.26b)$$

Rappelons enfin que $P_l(\cos \theta)$ représente le polynôme de Legendre et que θ est l'angle entre les directions de $\mathbf{k}$ et de $\mathbf{r}$. Les formules précédentes montrent que le potentiel de mélange ne perturbe que la partie $l=2$ de l'onde *s*.

2.5 Forme asymptotique des fonctions d'onde et expression des amplitudes de diffusion *T*

Afin de déterminer la résistivité électrique et la variation de densité électronique, nous aurons besoin de l'amplitude de diffusion; celle-ci sera déterminée à partir de la forme asymptotique des quantités J_s et J_{dm} . Nous obtenons aisément à l'aide de la méthode de la phase stationnaire [6, 16, 28] les relations suivantes:

$$J_s(E, \mathbf{r}) = \frac{\Omega}{(2\pi)^3} \frac{\pi m^*}{k} \nu^{sd}(k) e^{i(kr + \delta_2(k))} \quad (2.27a)$$

$$J_{dm}(E, \lambda) = \frac{\Omega}{2\pi} \frac{1}{1 - v^{dd} G^{0d}} \sum_j \alpha_{mj}^d \frac{e^{i\mathbf{k}_j \cdot \lambda}}{|\lambda|}. \quad (2.27b)$$

Dans l'expression (2.27b), les vecteurs $\mathbf{k}_j$ sont des vecteurs ayant leur extrémité sur la surface d'énergie E , tels que $\nabla_{\mathbf{k}_j} E = i\lambda$ ($i > 0$); les quantités α_{mj} sont définies par les relations:

$$\alpha_{mj} = \frac{re i \phi_j}{|\mathbf{r} \mathbf{A}_{mj}^{-1} \mathbf{r} \det \mathbf{A}_{mj}|^{1/2}} \quad (2.28)$$

$$\mathbf{A}_{mj} = (\nabla_{\mathbf{k}} \nabla_{\mathbf{k}} E_m(\mathbf{k}))_{\mathbf{k}=\mathbf{k}_j} \quad (2.29)$$

$$\phi_j = \begin{cases} 0 & \text{si } A_{mj} \text{ est défini positif} \\ \pi/2 & \text{si } A_{mj} \text{ est non défini} \\ \pi & \text{si } A_{mj} \text{ est défini négatif} \end{cases} \quad (2.30)$$

le lien entre la forme asymptotique des fonctions d'onde et l'amplitude de diffusion se déduit de l'équation de diffusion:

$$|\Psi_{nk}\rangle = |nk\rangle = \sum_{m,k'} \frac{T_{mk'}^{nk}}{E - E_{mk'}^0} |mk'\rangle \quad (2.31)$$

où la matrice T est définie par ses éléments de matrice:

$$T_{mk'}^{nk} = \langle mk' | V | \Psi_{nk} \rangle \quad (2.32)$$

la forme asymptotique de la fonction (2.31) s'écrit dans la base des fonctions du métal pur sous la forme [16]:

$$\lim_{r \rightarrow \infty} \Psi_{nk}(\mathbf{r}) = \langle \mathbf{r} | nk \rangle - \frac{\Omega}{2\pi r} \times \sum_{m, \mathbf{k}_i} \alpha_{mi} T_{m\mathbf{k}_i}^{nk} \langle \mathbf{r} | m\mathbf{k}_i \rangle. \quad (2.33)$$

Les quantités α_{mi} et $\mathbf{k}_i$ sont définies plus haut (cf. (2.28)). Par identification de la formule (2.31) avec les formules (2.24) et (2.25) exprimées dans la base du métal pur, nous obtenons l'amplitude de diffusion sur la couche d'énergie constante $E_k^0 = E_{k'}^0$:

$$T_{sk'}^{sk} = -\frac{\pi}{ikm^*} \sum_{l=0}^{\infty} (S_l^{ss}(k) - 1) \times (2l+1) P_l(\cos \theta_{\mathbf{k}\mathbf{k}'}) \quad (2.34a)$$

$$T_{dmk'}^{dmk} = \delta_{mm'} \frac{v^{dd} + G_1^{ds}}{(1 - v^{dd} G^{0d})(1 - G_1^d G_1^{ds})} \quad (2.34b)$$

$$T_{dmk'}^{sk} = -\frac{e^{i\delta_2(k)} \nu^{sd}(k) Y_2^m(\hat{k})}{k(1 - v^{dd} G^{0d})(1 - G_1^d G_1^{ds})}. \quad (2.34c)$$

Nous avons introduit explicitement la partie *s-s* de la matrice de diffusion: celle-ci a pour expression:

$$S_l^{ss}(k) = \begin{cases} e^{2i\delta_l(k)}, & l \neq 2 \\ e^{2i\delta_2(k)} \left(1 - 2i\pi \frac{n^{ds} G_1^{ds}}{1 - G_1^{ds} G_1^{ds}} \right), & l = 2. \end{cases} \quad (2.35)$$

Ce résultat nous servira dans les paragraphes suivants; cependant, nous pouvons dès à présent discuter le comportement différent des métaux nobles et des métaux de transition vis à vis de la diffusion s - d ; nous examinons dans la suite de ce paragraphe successivement ces deux cas.

2.5(a) *Amplitudes de diffusion dans le cas du métal noble* Les bandes d sont pleines dans un métal noble de sorte que le nombre de particules est conservé dans chaque canal: on doit avoir $|S_l^{ss}(k)| = 1$ [17] et l'on peut alors définir un déphasage réel $\delta_2(k)$ tenant compte explicitement du déphasage de mélange. En reportant les formules (2.15) (2.5) avec la condition $n^d(E) = 0$ dans (2.35b), nous obtenons,

$$\begin{aligned} \delta_l(k) &= \delta_l(k) & l \neq 2 \\ \delta_2(k) &= \delta_2(k) + \delta^{sd}(k) & l = 2 \end{aligned} \quad (2.36)$$

où δ^{sd} est le déphasage de mélange défini par (2.16). Dans le cas du métal noble, les déphasages apparaissant dans la forme asymptotique sont ceux qui apparaissent dans la charge déplacée et dans la variation de densité d'états, les relations classiques entre résistivité, variation de densité électronique... seront encore valables, pourvu que l'on remplace le déphasage $\delta_2(k)$ par le déphasage $\delta_2'(k)$ défini par (2.36).

2.5(b) *Amplitude de diffusion dans le cas d'un métal de transition.* Lorsque la matrice est un métal de transition, il n'y a plus conservation du nombre de particules dans chaque canal l puisque des particules s sont diffusées dans les bandes d par le potentiel de mélange. Dans ces conditions, le déphasage δ_2' est complexe, ainsi qu'il est naturel dans le cas d'un potentiel absorbant [17]. Afin de mettre en évidence le rôle de la bande d nous écrivons

la matrice S sous la forme:

$$S_2^{ss}(k) = e^{2i\delta_2'(k)} - 2i \left| \frac{G^{0d} G_1^{ds}}{1 - G^{0d}(v^{dd} + G_1^{ds})} \right| \times \sin(\delta^d + \phi^d) e^{i(2\delta_2 + \delta^{sd} - \delta^{sd})} \quad (2.37)$$

avec les notations:

$$\phi^{sd} = \text{Arg } G_1^{ds} = \text{Arctg}(-\pi n^{ds}/f^{ds}) \quad (2.38a)$$

$$\phi^d = \text{Arg } G^{0d} = \text{Arctg}(-\pi n^d/f^d) \quad (2.38b)$$

$$\delta^d = -\text{Arg}(1 - v^{dd} G^{0d}) = \text{Arctg}(-\pi v^{dd} n^d / (1 - v^{dd} f^d)). \quad (2.38c)$$

Les déphasages δ_l sont les déphasages dus au potentiel V^{ss} seul, $\delta_2(k)$ est défini par (2.36) et le déphasage δ^d est le déphasage introduit dans chaque bande d (cf. (2.19)). Le premier terme de (2.37) est celui qu'on aurait dans un métal noble ayant mêmes déphasages δ_2 et δ^{sd} ; le dernier terme est nul quand la bande d est pleine.

2.6 Résistivité résiduelle dans un alliage à base de métal noble ou de transition

Ainsi que nous l'avons remarqué dans le paragraphe précédent, la résistivité dans le cas d'un métal noble se réduit à la forme classique [5]:

$$\rho = \frac{4\pi}{A_s k_f} \sum_{l=1}^{\infty} \sin^2(\delta_l' - \delta_{l-1}') \quad (2.39)$$

pourvu qu'on l'écrive en fonction des déphasages δ_l' définis par (2.36) (A_s est le nombre d'électrons de conduction par atome du métal).

Il n'en est plus de même dans le cas d'un métal de transition puisque les bandes d et la bande s contribuent à la résistivité électrique. Il faut revenir à l'équation de Boltzmann. Le problème est ici entièrement soluble, parce que les amplitudes de diffusion (2.34) $T_{\mathbf{k}\mathbf{k}}^s$ ont une dépendance très particulière par rapport aux vecteurs $\mathbf{k}$ et $\mathbf{k}'$. $T_{\mathbf{k}\mathbf{k}}^s$ ne dépend que de l'angle entre $\mathbf{k}$ et $\mathbf{k}'$, $T_{\mathbf{k}\mathbf{k}}^{ds}$ ne dépend que de l'énergie de la diffusion (diffusion isotrope)

et T_{dk}^{sk} ne dépend que du vecteur $\mathbf{k}$. Nous obtenons alors aisément les expressions de la résistivité électrique (Appendice 2). Nous nous bornons ici à discuter les résultats obtenus pour les résistivités s et d .

2.6(a) *Résistivité de la bande s* . La résistivité s est dominante dans les métaux de transition; c'est la somme de trois contributions s dont on examinera successivement la nature:

$$\rho_s = \rho_{s1} + \rho_{s2} + \rho_{s3} \quad (2.41a)$$

(1) *Contribution de la bande s* . ρ_{s1} est la résistivité de la bande s supposée seule:

$$\rho_{s1} = \frac{4\pi}{A_s k_f} \sum_{l=1}^{\infty} \sin^2(\delta_l - \delta_{l-1}). \quad (2.42)$$

(2) *Contribution de la bande s due au mélange s - d seul*. Ce terme est le seul qui ne soit pas nul en l'absence de terme direct V^{ss} :

$$\rho_{s2} = \frac{2\pi}{A_s} \sum_m \langle |v_m^{sd}(\mathbf{k})|^2 \rangle \times \frac{n^d(E_f, \Gamma_m) + G^{0d}(E_f, \Gamma_m) n^{ds}(E, \Gamma_m)}{1 - G^{0d}(E_f, \Gamma_m) (v^{dd} + G_1^{ds}(E_f, \Gamma_m))} \quad (2.43)$$

ρ_{s2} est formellement identique au résultat obtenu par Gomès. Cependant, on doit remplacer dans la formule correspondante (cf. (13b)) Réf.[1] $|v^{sd}|^2$ par la moyenne sur la surface de Fermi de la quantité $|v_m^{sd}(\mathbf{k})|^2$. Cette moyenne est indépendante de m lorsque $V(\mathbf{r})$ a la symétrie sphérique, ce que nous supposons toujours dans le cadre de ce travail. Enfin, $G_1^{ds}(E)$ est renormalisé par le potentiel V^{ss} (voir (2.15)). Remarquons que dans ce cas, (2.42) a une interprétation simple: en effet, à partir de la fonction d'onde ρ_{s2} peut s'exprimer en fonction de la densité d'états d par unité d'énergie au niveau de Fermi et sur la cellule de l'impureté $n_d(E_f, 0)$:

$$\rho_{s2} = \frac{2\pi}{A_s} \langle |v_m^{sd}(\mathbf{k})|^2 \rangle n_d(E_f, 0). \quad (2.43)$$

(2.43) généralise la formule de Fermi au cas où le potentiel d'impureté n'est pas traité en perturbation: le potentiel $v^{sd}(\mathbf{k})$ induit des transitions s - d avec une probabilité donnée par la formule de Fermi où l'on remplace la densité d'états finale du métal non perturbé par la densité d'états du métal perturbé sur le site de l'impureté.

(3) *Contribution due aux potentiels V^{ss} et V^{sd}* . Le terme de mélange a une forme complexe:

$$\rho_{s3} = \frac{4\pi}{A_s k_f} \sin \psi_s [10 \sin \delta_2 \cos(\delta_2 + \delta^{sd} + \phi^d + \delta^d) - 4 \sin \delta_1 \cos(\delta^{sd} + \phi^d + \delta_2 - \delta_1) - 6 \sin \delta_3 \cos(\delta^{sd} + \phi^d + \delta_3 - \delta_2)] \quad (2.44)$$

avec:

$$\sin \psi_s = \frac{\pi n^{ds}}{\xi^2 + (v^{dd} + f^{ds} - 1/f \cos^2 \phi^d)^2}^{1/2} \quad (2.45a)$$

$$\zeta = \pi n^{ds} - \frac{\sin 2\phi^d}{2f^d}. \quad (2.45b)$$

La signification physique de ψ_s apparaîtra dans le paragraphe suivant.

2.6(b) *Résistivité due aux bandes d* . La résistivité due aux bandes d peut se calculer également à l'aide des résultats de l'Appendice 2. Les cinq bandes d étant indépendantes d'après les hypothèses du calcul que nous avons présenté. Les conductibilités σ_{dm} associées à chaque bande s'ajoutent et nous obtenons pour la résistivité de l'ensemble des bandes d :

$$\rho_{ds}^{-1} = e^2 \sum_m \langle v^2 \rangle_m n^d(E, \Gamma_m) \tau_{dm}(E_f)$$

$$\tau_{dm}^{-1}(E) = 2\pi \left\{ \left| \frac{v_{dm}^d + G_{1m}^{ds}}{1 - G^{0d}(v_{dm}^d + G_{1m}^{ds})} \right|^2 n_d(E, \Gamma_m) + \frac{\langle |v_m^{sd}(k)|^2 \rangle n_s(E_f)}{|1 - G_m^{0d}(v_{dm}^{d0} + G_m^{ds})|^2} \right\}$$

$\langle v^2 \rangle_m$ est la valeur moyenne du carré de la vitesse sur la surface de Fermi m . Le temps de relaxation $\tau_{dm}(E)$ se compose de deux termes: le premier traduit la diffusion à l'intérieur de la bande d compte tenu de l'hybridation s - d ; le second provient uniquement de l'hybridation.

Dans ces formules, nous avons conservé l'indice m bien que si les bandes d sont identiques, $\langle v^2 \rangle_m$, $n_d(E, \Gamma_m)$, G_{lm}^{ds} ... sont indépendants de m . La raison en est que, lorsque les cinq bandes d sont hybridées, il est facile de montrer que les formules sont identiques pourvu que la somme se fasse sur les orbitales m ($m = 1, \dots, 5$), tandis que $\langle v_m^2 \rangle$ mesure la moyenne de $v^2(k) |\langle m0 | i\hbar k \rangle|^2$ sur l'ensemble des surfaces de Fermi d ($i = 1, \dots, 5$). Notons que les formules (2.41b) exigent la connaissance détaillée des surfaces de Fermi d alors que les formules (2.41a) ne demandent que la connaissance de densités d'états.

2.7 Variation de densité électronique dans un alliage à base de métal noble ou de transition

La forme asymptotique de la densité électronique s'obtient aisément à partir de la forme asymptotique des fonctions d'onde (cf. (2.5)) [18]. Pour une surface de Fermi sphérique, l'amplitude de diffusion $T_{\mathbf{k}}^{\mathbf{k}'}$ ne dépend que de l'angle $\theta = (\mathbf{k}, \mathbf{k}')$ entre les vecteurs incident et diffusé; la forme asymptotique de la variation de densité électronique s s'écrit alors (cf. Appendice 1):

$$\Delta \rho^s(\mathbf{r}) = \frac{k_f m^*}{(2\pi)^3} u(r)^2 \frac{1}{r^3} \operatorname{Re} \{ T_s^s(\theta = \pi) e^{2ik_f r} \}. \quad (2.46)$$

Nous nous limitons dans la suite à l'étude de la variation de densité s ; la variation de densité d s'exprime de façon analogue à l'aide des coefficients α_{mi} définis par (2.28) (2.30).

Dans un alliage à base de métal noble, les formules classiques demeurent valables, pourvu qu'on remplace les déphasages δ_i par les déphasages δ'_i définis par (2.36):

$$\Delta \rho_n^s(\delta'_i, r) = -\frac{1}{4\pi^2 r^3} \sin \delta'_i \cos(2k_f r + \delta'_i). \quad (2.47)$$

Dans un alliage à base de métal de transition, il n'en est plus de même. Dans ce cas, $\Delta \rho^s(r)$ comprend deux termes:

$$\Delta \rho^s(r) = \Delta \rho_n^s(\delta'_i, r) + \Delta \rho_t^s(r). \quad (2.48)$$

Le premier, $\Delta \rho_n^s(\delta'_i, r)$ représente la variation de densité qu'on aurait dans un métal noble ayant les mêmes valeurs pour les déphasages δ'_i ; le second, $\Delta \rho_t^s(r)$ est caractéristique du métal de transition et s'annule pour des énergies telles que $n^d(E) = 0$:

$$\begin{aligned} \Delta \rho_t^s(r) &= \frac{k_f m^* u(r)^2}{(2\pi)^3 r^3} \sin(\phi^d + \delta^d) \\ &\times \left| \frac{G^{0d} G_1^{ds}}{1 - G^{0d}(v^{dd} + G_1^{ds})} \right| \\ &\times \cos(2k_f r + 2\delta_2 + \delta^{sd} - \phi^{sd}). \end{aligned} \quad (2.49)$$

L'amplitude et la phase de ce terme (2.49) dépendent de la structure de bandes du métal de transition; son importance est prédominante dans les cas où l'énergie de Fermi est proche d'une résonance (dd ou sd) nous nous proposons d'étudier ultérieurement l'importance de ce terme.

Nous pouvons également mettre en évidence l'effet de la bande d en réécrivant (2.48) sous une forme équivalente:

$$\Delta \rho^s(r) = \Delta \rho^s(\delta_i, r) + \Delta^{sd}(r) \quad (2.50a)$$

$$\begin{aligned} \Delta \rho^{sd}(r) &= -\frac{1}{4\pi^2} \sin \psi_s \\ &\times \frac{\cos(2k_f r + 2\delta_2 + \delta^{sd} + \delta^d + \delta^d)}{r^3}. \end{aligned} \quad (2.50b)$$

Le premier terme représente la variation de densité électronique dans la bande s supposée seule; le second mesure l'importance des termes de mélange et de la bande d . La formule (2.50) appelle d'ailleurs les commentaires suivants:— la phase des oscillations de densité n'a pas de relation immédiate avec le seul

déphasage de mélange δ^{sd} ; le fait que la bande soit incomplète introduit un déphasage ϕ^d indépendant du potentiel d'impureté; — l'amplitude des oscillations est réduite parce qu'une grande partie de l'écran se fait dans la bande *d*; c'est pourquoi, quel que soit le potentiel v^{dd} , $|\sin \Psi_s|$ ne peut atteindre la valeur limite unité, même pour une énergie correspondant à une résonance. Le maximum de $\sin \psi_s$ est donné par:

$$\sup \sin \Psi_s = \frac{\pi n^{ds}}{[(\pi n^{ds})^2 + \frac{\sin^2 \phi^d}{f^2} (3 - \sin^2 \phi^d)]^{1/2}} \quad (2.51)$$

il est d'autant plus faible que la densité d'états *d* est plus grande.

2.8 Polarisation de spin introduite par une impureté dans un métal noble

L'importance des formules précédentes est grande dans l'étude de la polarisation de spin introduite par une impureté magnétique. Nous nous contentons de discuter le cas d'une impureté dans un métal noble.

Lorsque l'impureté est magnétique, dans l'approximation de Hartree-Fock, le potentiel d'impureté dépend du spin; les grandeurs précédemment étudiées, en particulier $\Delta \rho^s(r)$, sont relatives à une direction de spin donnée. La polarisation de spin *s* introduite par une impureté magnétique vaut simplement:

$$\Delta m_i^s(r) = \Delta \rho_i^s(r) - \Delta \rho_i^s(r) \quad (2.52)$$

la contribution de la diffusion à la polarisation de spin s'écrit alors:

$$\Delta m_i^s(r) = -\frac{1}{4\pi^2} \sin(\delta'_{i\uparrow} - \delta'_{i\downarrow}) \times \frac{\cos(2k_f r + \delta'_{i\uparrow} + \delta'_{i\downarrow})}{r^3} \quad (2.53)$$

Nous supposons que seuls les éléments de matrice v^{dd} dépendent du spin de façon significative[9]; les formules précédentes per-

mettent alors d'obtenir:

$$\Delta m_i^s(r) = -\frac{1}{4\pi^2} \sin(\delta'_{i\uparrow} - \delta'_{i\downarrow}) \times \frac{\cos(2k_f r + 2\delta_2 + \delta'_{i\uparrow} + \delta'_{i\downarrow})}{r^3} \quad (2.54)$$

L'amplitude des oscillations *s* a la même forme que lorsqu'il n'existe pas de diffusion *s-s*; la phase est modifiée par le facteur $2\delta_2$.

A ce facteur de phase près, la polarisation de spin est identique à celle que donnerait un hamiltonien du type Kondo avec une intégrale d'échange effective[19, 20]

$$J_m(\mathbf{k}, \mathbf{k}') = \frac{v_m^{s\mathbf{k}} v_m^{s\mathbf{k}'}}{(E - E_{i\uparrow})(E - E_{i\downarrow})} \quad (2.55)$$

Celle-ci dépend implicitement de V^{ss} puisque $v^{sd}(\mathbf{k})$ est renormalisé par la diffusion *s-s*: (cf. (2.13)). Nous retrouvons ainsi le résultat obtenu par la transformation de Schrieffer-Wolff[20, 21] au facteur de phase $2\delta_2$ près.

3. CONCLUSION

Dans cet article, nous avons développé la théorie formelle de l'effet de l'hybridation *s-d* introduite par une impureté de transition dans une matrice à base de métal noble ou de transition; nous avons étudié en détail un modèle simple directement applicable aux alliages à base de cuivre ou de nickel. L'analyse en déphasages a été étendue au type d'alliages considérés pour le calcul des différentes propriétés physiques (résistivité, variation de densité électronique, polarisation de spin *s* etc...). Ces résultats seront appliqués aux alliages à base de cuivre[8] ou de nickel. Enfin, nous comptons étendre ce formalisme au cas où l'hybridation *s-d* due à la matrice n'est pas négligeable.

REFERENCES

1. GOMES A. A. J. *Phys. Chem. Solids*, **27**, 451 (1966).
2. CAMPBELL I. A. and GOMES A. A. *Proc. phys. Soc.*, **2**, 1312 (1968).

3. HUBBARD J., *Proc. phys. Soc.* **92**, 921 (1967).
4. MUELLER F. M., *Phys. Rev.* **153**, 659 (1967).
5. FRIEDEL J., *Nuovo Cim.* **7**, 287 (1958).
6. SLATER J. C. and KOSTER G. E., *Phys. Rev.* **95**, 1167 (1954).
7. FRIEDEL J., GAUTIER F., GOMES A. A. and LENGART P., *Quantum Theory of Atoms, Molecules and the Solid State* (Edited by O. Lowdin), p. 445. Academic Press, New York (1966).
- 7a. GAUTIER F. and LENGART P., *Phys. Rev.* **139A**, 705 (1965).
8. RIEDINGER R., à paraître.
9. ANDERSON P. W., *Phys. Rev.* **124**, 41 (1961).
10. FRIEDEL J., *J. phys. Radium* **23**, 693 (1962).
10. WOLFF P. A., *Phys. Rev.* **124**, 1036 (1961).
10. CLOGSTON A. M., *Phys. Rev.* **129**, 168 (1962).
11. HIRSCHITZ F., *Adv. Phys.* **13**, 483 (1964).
12. CALLAWAY J., *J. math. Phys.* **5**, 783 (1964).
13. BLANDIN A., *J. phys. Radium* **22**, 505 (1961).
14. MESSIAH A., *Mécanique Quantique*. Dunod (1964).
15. KOHN W. and LUTTINGER J. M., *Phys. Rev.* **97**, 869 (1955).
16. RIEDINGER R., *Thèse de 3me cycle*. Strasbourg (1969).
17. MOIT and MASSI Y., *Theory of Atomic Collisions*. Clarendon Press, Oxford (1965).
18. BLANDIN A., *Thèse*, Paris (1961).
19. BLANDIN A., *J. appl. Phys.* **39**, 1285 (1968).
20. WOLFF P. A. and SCHRIEFFER P., *Phys. Rev.* **149**, 491 (1966).
21. APPELBAUM J. A. and KONDO J., *Phys. Rev.* **170**, 549 (1968).
21. LOULOUSE G., COQUELIN B., *Solid State Commun.* **7**, 853 (1969).
22. ZIMAN J. M., *Electrons and Phonons*. Oxford University Press, Oxford (1963).
23. KANAMORI J., *J. appl. Phys.* **36**, 929 (1965).
24. BURDICK G. A., *Phys. Rev.* **129**, 168 (1962).
25. SOKOLOFF J. B., *Phys. Rev.* **161**, 540 (1967).
26. DURAND J., *Thèse de 3me cycle*, Strasbourg (1969).
27. DEMANGEAT C., *Thèse de 3me cycle*, Strasbourg (1969).
28. MANN F., *Phys. Status Solidi* **11**, 753, **11**, 767, **13**, 293 (1965).

APPENDICE I

Forme asymptotique de la variation de charge

Nous généralisons ici les formules obtenues par Blandin [13] dans le cas de plusieurs bandes. La variation de densité électronique pour une valeur du vecteur $\mathbf{k}$ donnée est:

$$\Delta\rho(\mathbf{k}, \mathbf{r}) = \sum_n |\psi^{nk}(\mathbf{r})|^2 - |\phi^{nk}(\mathbf{r})|^2$$

Grâce aux équations (2.33) nous pouvons la mettre sous la forme suivante:

$$\Delta\rho(\mathbf{k}, \mathbf{r}) = \sum_{m \neq n} \Delta\rho^{nm}(\mathbf{k}, \mathbf{r}) + \sum_{m \neq n} \Delta\rho^{nm}(\mathbf{k}, \mathbf{r})$$

Nous obtenons des densités de symétrie bien définie, n , et des densités hybrides. Ces dernières sont négligeables, car leur contribution est nulle en moyenne sur une cellule Ω_k à grande distance de l'impureté; en effet, avec les définitions (2.28) à (2.30).

$$\int_{\Omega_k} \Delta\rho^{nm}(\mathbf{k}, \mathbf{r}) d^3r = \int_{\Omega_k} \frac{\alpha_{nk}}{r} \frac{\alpha_{mk}}{r} \phi^{nk}(\mathbf{r}) \phi^{mk}(\mathbf{r}) d^3r \\ = \int_{\Omega_k} \phi^{nk}(\mathbf{r}) \phi^{mk}(\mathbf{r}) d^3r = \delta_{nm} \delta_{\mathbf{k}, \mathbf{k}_i}$$

d'après l'orthogonalité des fonctions de Bloch.

La variation pour une bande donnée et une énergie donnée de la densité électronique sera donc:

$$\Delta\rho^n(E, \mathbf{r}) = -\frac{\Omega}{(2\pi)^3} \left\{ \left[-\frac{1}{2\pi} \int_{S_n(E)} \frac{dSk}{|\nabla_k E|} \sum_{k_i} T_{nk, k_i}^{nk} \frac{\alpha_{nk}^*}{r} \right. \right. \\ \times \phi^{nk}(\mathbf{r}) \phi^{nk}(\mathbf{r}) + cc \left. \right] + \frac{1}{4\pi^2} \sum_{i,j} \frac{\alpha_{ni} \alpha_{nj}}{r^2} \\ \times \left[\sum_m \int_{S_n(E)} \frac{dSk}{|\nabla_k E|} T_{nk, k_i}^{mk} T_{nk, k_j}^{mk*} \right] \phi^{nk}(\mathbf{r}) \phi^{nk}(\mathbf{r}) \left. \right\}$$

$S_n(E)$ est la surface d'énergie constante relative à la bande n . Le premier terme s'évalue aisément d'après la méthode de la phase stationnaire. Nous obtenons:

$$I = \int_{S_n(E)} \frac{dSk}{|\nabla_k E|} \sum_{k_i} T_{nk, k_i}^{nk} \alpha_{ni} \phi^{nk}(\mathbf{r}) \phi^{nk}(\mathbf{r}) + cc \\ = \frac{2\pi}{n} [\alpha_{ni} T_{nk, k_i}^{nk} \phi^{nk}(\mathbf{r}) - \alpha_{ni} T_{n-k, k_i}^{n-k} \phi^{n-k}(\mathbf{r})]$$

avec la définition de T , le second s'écrit:

$$J = \sum_m \int_{S_n(E)} \frac{dSk}{|\nabla_k E|} T_{nk, k_i}^{mk} T_{nk, k_j}^{mk*} = \sum_m \int_{S_n(E)} \frac{dSk}{|\nabla_k E|} \\ \times \langle \phi^{nk} | V | \psi^{mk} \rangle \langle \psi^{mk} | V | \phi^{nk} \rangle$$

cette expression peut se simplifier à l'aide d'une généralisation du théorème optique; en utilisant la définition de l'opérateur G ,

$$G = \sum \frac{|\psi^{nk}\rangle \langle \psi^{nk}|}{E^+ - E_{nk}}, \text{ nous obtenons:}$$

$$J = \frac{(2\pi)}{\Omega} \left\langle \phi^{nk} | V | \frac{G^+ - G^-}{-2\pi i} | V | \phi^{nk} \right\rangle$$

avec l'équation de diffusion, $|\Psi\rangle = |\phi\rangle + GV|\phi\rangle$ et la définition (2.32) il vient:

$$J = \frac{2\pi}{i} \{ T_{nk, k_i}^{nk} - T_{nk, k_i}^{nk*} \}.$$

En regroupant les deux types de termes I et J , la variation de densité $\Delta\rho^n(E, \mathbf{r})$ devient:

$$\Delta\rho^n(E, \mathbf{r}) = -\frac{\Omega_0}{(2\pi)^3 i r^2} \\ \times \left\{ \sum_{k_i, k_j} \alpha_{ni} \alpha_{nj} \phi^{nk_i}(\mathbf{r}) \phi^{nk_j}(\mathbf{r}) T_{n-k_i, k_j}^{n-k_i} - cc \right\}$$

la variation totale de charge électronique par bande et par spin σ s'obtient en intégrant la relation précédente jusqu'au niveau de Fermi

$$\Delta \rho_{\sigma}^n(\mathbf{r}) = \frac{\Omega_0}{(2\pi)^3 r^3} \sum_{k_i, k_j} \times \frac{\alpha_{n_i} \alpha_{n_j} \phi^{n k_i}(\mathbf{r}) \phi^{n k_j}(\mathbf{r}) T_{n k_i}^{n-k_j} + c.c.}{\frac{1}{|\nabla_k E n|_i} + \frac{1}{|\nabla_k E n|_j}} + 0 \left(\frac{1}{r^4} \right).$$

On remarquera notamment que seules les amplitudes de diffusion T_{n}^n interviennent dans l'expression finale de la variation de densité de type n .

APPENDICE 2

Résistivité électrique dans un modèle à plusieurs bandes

L'intégrale de collision associée à la diffusion d'un électron $m\mathbf{k}$ ($m = s, di$) est donnée par [22]:

$$\frac{\partial f_m}{\partial t}(\mathbf{k})|_{\text{coll}} = \sum_n \int P_{n\mathbf{k}}^{m\mathbf{k}} (g_m(\mathbf{k}) - g_n(\mathbf{k}')) d\mathbf{k}' \quad (\text{A2.1})$$

où $g_m(\mathbf{k})$ est l'écart de la fonction de distribution par rapport à l'équilibre résultant de l'application d'un champ électrique. $P_{n\mathbf{k}}^{m\mathbf{k}}$ est la densité de probabilité de transition pour qu'un électron $m\mathbf{k}$ soit diffusé en $n\mathbf{k}'$; celle-ci est reliée à la matrice T (cf. (2.32)) par:

$$P_{n\mathbf{k}}^{m\mathbf{k}} = \frac{1}{(2\pi)^2} |T_{n\mathbf{k}}^{m\mathbf{k}}|^2 \delta(E_k - E_{k'}) \quad (\text{A2.2})$$

nous cherchons des solutions du type:

$$g_m(\mathbf{k}) = -\frac{\partial f^0}{\partial E} \tau_m(\mathbf{k}) \mathbf{v}_m(\mathbf{k}) \cdot \mathcal{E} \quad (\text{A2.3})$$

où $\mathbf{v}_m(\mathbf{k})$ est la vitesse de l'électron $n\mathbf{k}$ et f^0 la fonction de distribution de Fermi Dirac. S'il existe une telle solution aux équations de Boltzmann relatives à chaque bande m , le courant total est la somme des courants j_m transportés par chaque bande m et nous obtenons:

$$j_m = \sigma_m \mathcal{E} = \frac{e^2}{8\pi^3} \int_{S_m(E_F)} \tau_m(\mathbf{k}) \mathbf{v}_m(\mathbf{k}) (\mathbf{v}_m(\mathbf{k}) \cdot \mathcal{E}) \frac{dS_k}{v_m(k)} \quad (\text{A2.4})$$

l'intégrale étant effectuée sur la surface de Fermi relative à la bande m .

En général, les équations de Boltzmann relatives à chaque bande m sont couplées par les termes $m \neq n$ de (A2.1). Dans notre cas particulier (cf. (2.34)) ces termes de couplage sont nuls par raison de symétrie:

(1) pour $m = di$, $n = s$, l'intégrale de (A2.1) se fait sur une surface sphérique et l'intégrale de $|Y_l^m(k')|^2 \mathbf{k} \cdot \mathcal{E}$ est nulle;

(2) pour $m = s$, ou di , $n = di$, l'intégrale se fait sur une surface $S_n(E_F)$ quelconque mais la probabilité de transition est indépendante de $\mathbf{k}'$; l'intégrale se réduit à l'intégrale de $v_m(\mathbf{k}')$ sur $S_m(E_F)$; celle-ci est nulle pour une surface de Fermi centrosymétrique [1].

Les intégrales de collision se réduisent alors à:

$$\begin{aligned} \frac{\partial f_m}{\partial t}|_{\text{coll}} &= \int_{S_m(E_F)} P_{m\mathbf{k}}^{m\mathbf{k}} (g_m(\mathbf{k}) - g_m(\mathbf{k}')) \frac{dS_k'}{v_m(\mathbf{k}')} \\ &+ g_m(\mathbf{k}) \sum_{n \neq m} \frac{1}{\tau_{mn}(\mathbf{k})} \end{aligned} \quad (\text{A2.5})$$

avec:

$$\tau_{mn}^{-1}(\mathbf{k}) = \int_{S_n(E_F)} \frac{dS_k'}{v_n(\mathbf{k}')} P_{n\mathbf{k}}^{m\mathbf{k}}; \quad (m, n = s, di). \quad (\text{A2.6})$$

Dans les hypothèses que nous avons adoptées, il existe un temps de relaxation intrabande. En effet, (1) pour la bande s , la surface étant sphérique, nous obtenons pour $\tau_{ss}(\mathbf{k})$ le temps de relaxation classique [22]. (2) pour chaque bande di , $P_{di\mathbf{k}}^{di\mathbf{k}}$ ne dépend que de l'énergie et $\tau_{di di}(\mathbf{k})$ se réduit à l'expressions (A2.6).

Nous obtenons ainsi le temps de relaxation $\tau_m(\mathbf{k})$ sous la forme:

$$\frac{1}{\tau_m(k)} = \sum \frac{1}{\tau_{mn}(\mathbf{k})} \quad (m, n = s, di) \quad (\text{A2.7})$$

et la résistivité est alors obtenue à l'aide de (A2.4).

CLUSTER THEORY OF SOLUTIONS

A. N. MEN', M. P. BOGDANOVIĆ, JU. P. VOROBYOV, R. JU. DOBROVINSKI and
G. J. CHUFAROV

Academy of Sciences, Ural Branch, Institute of Metallurgy, Sverdlovsk, USSR

(Received 14 July 1969; in revised form 14 October 1969)

Abstract – The method of cluster components (*MCC*) is proposed. Using *MCC*, variations of several properties of solutions are interpreted as a function of concentration, including spinel solid solutions, metallic and ordering binary alloys.

1. INTRODUCTION

AT THE present time, a large amount of experimental data has been gained on composition–property relations for a broad class of solids and liquid melts, solutions, salt solutions, metallic alloys, etc. The main difficulty involved in the theoretical interpretation of the property–composition relation is that no strict quantum–mechanical calculations can be made in these complicated systems. This leads to the fact that in an overwhelming majority of cases simplified models are used on the basis of which phenomenological expressions for a functional property–composition relation can be written down, parameters of those being found by a semi-empirical method. At this point, there is a natural trend to describe the relation between different properties and concentration in terms of simpler functions. As the first and most widespread approximation, a linear property–composition relation is commonly used. A simple example of this approach provides Végard's law, employed for describing a lattice parameter as a function of concentration.

To realize such a phenomenological approach, it appears wise to utilize the equations, sometimes available for pure components, assuming that in describing the properties of solutions, it would be sufficient to retain the form of the equation, replacing the parameters therein by a linear combination of the parameters of the pure components, each weighted

by the mole fraction of the corresponding component; 'approximation through parameters' *ATP*.

By way of illustration we refer to calculations of activities vs. concentration which have been made for components in the MeO-type binary solutions[1].

The physical meaning of this *ATP* arises from an assumed mode of interaction between particles in a solution. Linear approximation evidences the additive nature of the concentration dependence of the appropriate parameter. If one succeeds in representing the property–concentration relationship in terms of a linear function, it can be said that one deals with a non-interacting system of components (with respect to this property) because the contribution of any component to the total amount is determined by multiplying the concentration of this component in the solution by the respective value, characterizing this property for a pure component.

In order to characterize the given property of solutions, it seems convenient to introduce the function of mixing Δx [2]

$$\Delta x = x_{sol} - \sum_i c_i x_{sol} (c_i \equiv 1, j, 0), \quad (1)$$

where C_i is concentration of the i -th component in the solution. If the function $x_{sol}(c_1, c_2, c_3)$ were known, one would be able to estimate the validity of *ATP*. In practice, however, as stated above, we know at best only functions $x_i = x_s$ ($c_i = 1, c_j = 0$), with

components not only pure substances but more complicated components as well, for example, $B^{(2)}(AB^{(1)})O_4$, $B^{(1)}(AB^{(2)})O_4$ when several components are hypothetical in the sense that no compounds of such composition with a given cation distributions exist in the pure state. We note that formulae (4)–(12) may be used to consider respective alloys of the type $Me^I Me_2^{II}$ with one common metal $A_{1-c}^I A_{1-c}^{II} B_2$ or $AB_{2(1-c)}^I B_{2c}^{II}$.

BINARY ORDERING ALLOYS

We now consider a binary ordering alloy containing two sublattices with an equal number of sites, for which the distribution matrix is

$$\begin{pmatrix} A & B \\ c + \lambda - 1/2 & 1 - c - \lambda \\ 1/2 - \lambda & \lambda \end{pmatrix}.$$

We select the following four independent structures as components

$$\begin{aligned} A_{1/2}^I A_{1/2}^{II} &\rightarrow \begin{pmatrix} 1/2 & 0 \\ 1/2 & 0 \end{pmatrix}; & A_{1/2}^I B_{1/2}^{II} &\rightarrow \begin{pmatrix} 1/2 & 0 \\ 0 & 1/2 \end{pmatrix}; \\ B_{1/2}^I B_{1/2}^{II} &\rightarrow \begin{pmatrix} 0 & 1/2 \\ 0 & 1/2 \end{pmatrix}; & B_{1/2}^I A_{1/2}^{II} &\rightarrow \begin{pmatrix} 0 & 1/2 \\ 1/2 & 0 \end{pmatrix}, \end{aligned} \quad (13)$$

with the aid of which it becomes possible to describe the matrix expansion of an alloy for different relations between λ and c .

Case 1: $\lambda < 1/2(1 - c)$

$$\begin{pmatrix} 1/2c & 1/2(1 - c) \\ 1/2c & 1/2(1 - c) \end{pmatrix} = cA_{1/2}^I A_{1/2}^{II} + (1 - c)B_{1/2}^I B_{1/2}^{II}. \quad (14)$$

Case 2: $\lambda > 1/2(1 - c)$

$$\begin{pmatrix} c + \lambda - 1/2 & 1 - c - \lambda \\ 1/2 - \lambda & \lambda \end{pmatrix} = (1 - 2\lambda)A_{1/2}^I A_{1/2}^{II} + 4[\lambda - 1/2(1 - c)]A_{1/2}^I B_{1/2}^{II} + 2(1 - c - \lambda)B_{1/2}^I B_{1/2}^{II}. \quad (15)$$

Case 3: $\lambda < 1/2(1 - c)$

$$\begin{pmatrix} c + \lambda - 1/2 & 1 - c - \lambda \\ 1/2 - \lambda & \lambda \end{pmatrix} = (2c + 2\lambda - 1)A_{1/2}^I A_{1/2}^{II} + 4[1/2(1 - c) - \lambda]B_{1/2}^I A_{1/2}^{II} + 2\lambda B_{1/2}^I B_{1/2}^{II}. \quad (16)$$

As may be seen from (14) to (16), the expansion is largely dependent on the difference $\lambda - 1/2(1 - c)$. If coefficients in the expansion are assumed to be non-negative (this condition is included in the general theoretical treatment and has a physical meaning), then we can estimate the existence region of the function $\lambda(c)$ (see Fig. 1) for each of the three cases.

Let us next consider the concentration dependence of various physical properties of solid solutions. We discuss primarily those of them to which a linear approximation can be applied on the basis of components determined in this section. This method will be further referred to as the method of cluster components MCC. The basic idea of the method resides in the fact that the property under investigation is conceived as a sum of contributions from each of the cluster components. The number of clusters coincides with the coefficient in the expansion of solution matrix into a sum of matrices of cluster components.

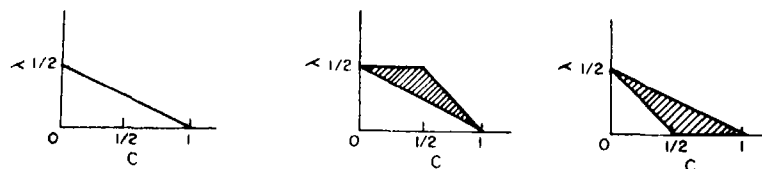


Fig. 1. The existence region of the function for a binary alloy $A_{1-c}B_c$ (1) Case 1 (13), Case 2 (14), Case 3 (15).

2. STRUCTURAL PARAMETERS AND MAGNETIC MOMENT IN SPINEL SOLID SOLUTIONS

Consider the concentration dependence of the structural parameters (the lattice constant a , the degree of inversion λ , and the oxygen parameter u in spinel solid solutions of the type 3a and 3b) by the d.c. method.

Oxygen parameter and crystal lattice parameter

In MCC, the lattice parameter of the solid solution is described by the expression

$$a(c) = \lambda_1 a_1 + (c - \lambda_1) a_2 + \lambda_2 a_3 + (1 - c - \lambda_2) a_4 \quad (17)$$

derived from (5), where a_i are the lattice parameters of the chosen components:

$$\begin{aligned} a_1 &\equiv \alpha_{A^{(1)}(B_1)O_4}; & a_2 &\equiv \alpha_{B(A^{(1)}B)O_4}; \\ a_3 &\equiv \alpha_{A^{(2)}(B_2)O_4}; & a_4 &\equiv \alpha_{B(A^{(2)}B)O_4}. \end{aligned} \quad (18)$$

Using experimental values of $a(c)$ and $\lambda_i(c)$, we can determine values of (18) from (17). On the other hand, with known values of a_i and $a(c)$, we can find $\lambda_i(c)$.

For the solid solution $A_c\text{Cd}_{1-c}\text{Fe}_2\text{O}_4$, where $A \equiv \text{Fe}^{2+}$, Co^{2+} from (17) at $A \equiv A^{(1)}$; $\text{Cd}^{2+} \equiv A^{(2)}$; $\text{Fe}^{3+} \equiv B$; $\lambda_1 \equiv O$, $\lambda_2 \equiv \lambda$ we obtain:

$$a(c) = ca_2 + \lambda a_3 + (1 - c - \lambda)a_4, \quad (19)$$

where a_2 , a_3 and a_4 are crystal lattice parameters of the inverted ferrite $\text{Fe}^{3+}(\text{AFe}^{3+})\text{O}_4$, normal ferrite $\text{Cd}^{2+}(\text{Fe}^{2+})\text{O}_4$ and hypothetical inverted cadmium ferrite $\text{Fe}^{3+}(\text{Cd}^{2+}\text{Fe}^{3+})\text{O}_4$, respectively. Using experimental data[6] $a(c)$ and $\lambda(c)$ for the system $\text{Fe}_c\text{Cd}_{1-c}\text{Fe}_2\text{O}_4$, we find $a_4 = 8,562 \text{ \AA}$.

Using the experimental $\lambda(c)$ the calculated value of $a(c)$ agrees well with experiment (Fig. 2).

We use the expression (19) to find $\lambda(c)$ from $a(c)$ in the system $\text{Co}_c\text{Cd}_{1-c}\text{Fe}_2\text{O}_4$ (Fig. 3).

As may be seen from Fig. 3, the agreement

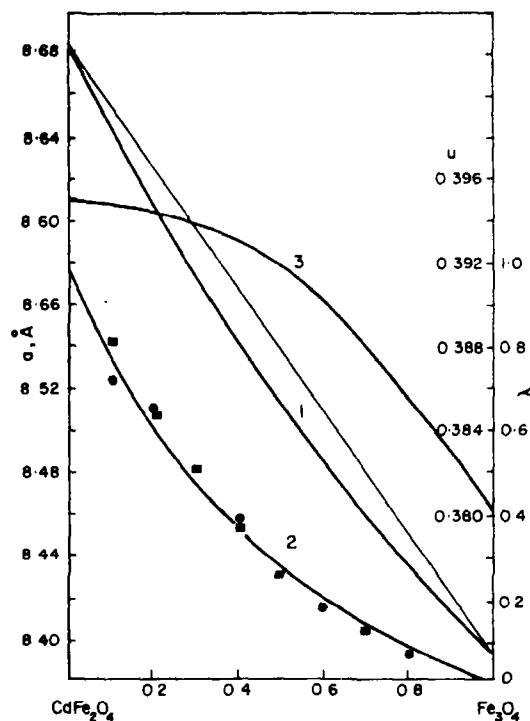


Fig. 2. Structural parameters for the system $\text{Fe}_c\text{Cd}_{1-c}\text{Fe}_2\text{O}_4$ as a function of concentration (c) $a(1)$, $\lambda(2)$, $u(3)$ solid lines — Experiment, points — calculation.

between the calculated and experimental $\lambda(c)$ is rather good.

Analogous calculations of $\lambda(c)$ for solutions $A\text{Fe}_2\text{CoCr}_{2(1-c)}\text{O}_4$, where $A \equiv \text{Fe}^{2+}$, Ni^{2+} were performed in paper[7] using both experimental values of $a(c)$ and λ for one composition of these solutions and expressions of the type (17) and a_i being substituted for $u(c)$ and u_i , can be utilized for calculation of u_i and $\lambda(c)$. For systems $A_c\text{Cd}_{1-c}\text{Fe}_2\text{O}_4$, where $A \equiv \text{Fe}^{2+}$, Co^{2+} , $u_4 = 0,411$ (see Figs. 2 and 3).

3. CONCENTRATION DEPENDENCE OF THE MAGNETIC MOMENT IN SPINEL SOLUTIONS

The method CC can be also applied to the interpretation of the concentration dependence of the magnetic moment of solutions. Thus, in particular, according to (11) and (12), the

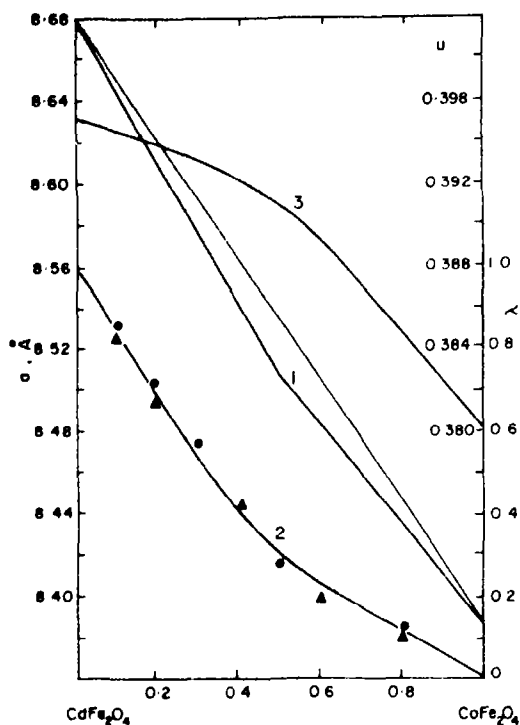


Fig. 3. Structural parameters for the system $\text{Co}(\text{Cd})_{1-c}\text{Fe}_2\text{O}_4$ as a function of concentration $a(c)$ (1), $\lambda(c)$ (2), $\mu(c)$ (3) (solid lines — experiment, points — calculation).

magnetic moment for a spinel solution of the type (13b) can be presented as $\lambda = c$

$$\mu(c) = (1 - \lambda)\mu_1 + c\mu_2 + (\lambda - c)\mu_3, \quad \lambda = c \quad (20)$$

$$\mu(c) = (1 - 2c + \lambda)\mu_1 + \lambda\mu_2 + 2(c - \lambda)\mu_3,$$

where

$$\begin{aligned} \mu_1 &\equiv \mu_{B^{IV}(4B^{IV})O_1}; & \mu_2 &\equiv \mu_{(B^{IV})O_1}; \\ \mu_3 &\equiv \mu_{A(B^{IV})O_1}; & \mu_4 &\equiv \mu_{B^{IV}(4B^{IV})O_1}, \end{aligned} \quad (21)$$

c means concentration of the normal component with the magnetic moment μ_2 . Since expression (20) contains both the unknown magnetic moments of the hypothetical com-

ponents, μ_3 and μ_4 , and an unknown function $\lambda(c)$, it is necessary, in order to find them, to have the property-composition relationship, particularly $a(c)$.

A self-consistent calculation of $\lambda(c)$, μ_4 , a_1 has been performed for the system $\text{NiFe}_{2(1-c)}\text{Rh}_{2c}\text{O}_4$ using the relation between $a(c)$ and $\mu(c)$ [8]. As a result we obtained $\mu_1 = -2\mu_B$ and $a_3 = 8.379 \text{ \AA}$ and $\mu(c)$ pictured in Fig. 4 (curve 3). Unfortunately, the lack of experimental data prevents us from making comparison.

DISCUSSION

The examples cited in Sections 2 and 3 form a reasonable basis for a more detailed discus-

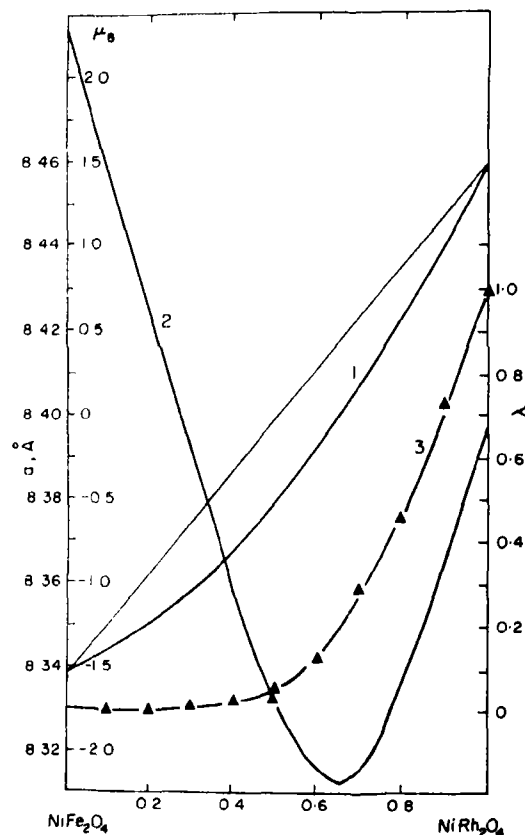


Fig. 4. Concentrational dependence of the crystal parameter, a (1); the magnetic moment, μ (2); and the degree of inversion, λ (3) for the solution $\text{NiFe}_{2(1-c)}\text{Rh}_{2c}\text{O}_4$.

sion of the cluster model of solutions itself, as well as the possibilities of its applications to the interpretation of the concentration dependence of various physical and physico-chemical properties of solutions and melts in a broad sense.

The principle point of this model is choosing cluster components capable of describing the concentration dependence of the property x under examination.

If the cluster components are properly chosen, the function of mixing[1] will be identically equal to zero and this may provide the criterion of the choice. With such a set of cluster components, the solution represents a gas composed of non-interacting particles, all the interactions being taken into account both in the choice of the set of components itself and in the expansion coefficients.

For a more complete solution of the particular problems, it seems desirable to have more data whose relation to concentration is defined by the same unknown composition functions which enter the coefficients of the solution matrix expansion into cluster compounds (the function $\lambda(c)$ may serve as analogue) and parameters characterising the respective property of the given cluster component. Then, an independent problem for a system of equations must be solved.

A simple example of this problem has been examined in Section 2, where using the experimental data $a(c)$ and $\mu(c)$ for the system $NiFe_{2(1-c)}Rh_{2c}O_4$ a degree of inversion vs. concentration, the size of the lattice parameter and the magnetic moment have been found d.c. $Fe^{3+}(Ni^{2+}Rh_{3+})O_4$.

It should be noted that in most cases, from the very form of CC it can be concluded what kind of solutions is to considered in order to find, with fewer equations, all the necessary parameters and functions. Thus for example, for the solid solution $A_cCd_{1-c}Fe_2O_4$, examined in Section 2, the lattice parameter CC of an inverted cadmium

ferrite has been found in the system $A \equiv Fe$ and already used for $A \equiv Co$. It can also be used for any other systems containing among CC an inverted cadmium ferrite. The proposed method (MCC) permits one to both explain the physical and physico-chemical properties of solid solutions and to find the parameters of its components.

CONCLUSIONS

(1) A general scheme is proposed of choosing cluster components for complicated solid solutions containing defectiveness and non-equivalent sites.

(2) Expansions of the solution matrix into a sum of matrices of cluster components are given for the case of the spinel solid solution with a common di- or trivalent cation, binary ordering alloy.

(3) The concentration dependence of the degree of inversion in several spinel solutions as well as the following parameters have been determined: the crystalline lattice parameters, the oxygen parameter and the magnetic moment in hypothetical cluster components.

REFERENCES

1. ZURAVLYOVA M. G., MEN' A. N. and CHUFAROV G. J. *Proc. acad. Sci. USSR* **159**, No. 4879, (1964).
2. MEN' A. N., BOGDANOVIĆ M. P., VOROBOV JU. P., ZURAVLYOVA M. G. and CHUFAROV G. J. *J. Phys. Chem. (USSR)* **43**, (1969).
3. MEN' A. N., KURUSHIN Yu. N., ZURAVLYOVA M. G., CHUFAROV G. J. *Proc. Acad. Sci. USSR* **175**, 132, (1967).
4. MEN' A. N. *Fiz. metall. (FMM)*, **7**, 638, (1959).
5. MEN' A. N. *(FMM)*, **9**, 801, (1960).
6. ILYINOVA G. N., BOGDANOVIĆ M. P., VOROBOV JU. P., MEN' A. N., POPOV G. P. and CHUFAROV G. J. *Cristallography* (in print).
7. MEN' A. N., BOGDANOVIĆ M. P., VOROBOV JU. P. and CHUFAROV G. J., *Proc. Acad. Sci. USSR* **186**, 1355, (1969).
8. BLASSE J. *Cristallognim. chpin. M.* (1968).

ESR-SPECTRA OF SODIUM-TITANIUM-SILICATE GLASSES AND OF TITANIUM-CONTAINING OXIDE COMPOUNDS

H. BÖHM and G. BAYER

Institut für Kristallographie und Petrographie Eidg. Techn. Hochschule, Zurich, Switzerland

(Received 14 August 1969)

Abstract—The formation of trivalent titanium in glasses and its dependence on chemical composition, temperature, atmosphere and irradiation were studied by means of ESR. For comparison and assignment of the resonances several crystalline titanium-containing oxide compounds were also investigated after slight reduction at 600°C in hydrogen.

1. INTRODUCTION

MANY titanium-containing glasses exhibit a special crystallization behavior. Our investigations[1,2] showed that the catalytic effect of titania on the crystallization of silicate glasses is due to phase separation and probably to formation of Ti^{3+} which is incorporated in the primary crystalline phase. The formation of Ti^{3+} also occurs in an oxidizing atmosphere if the melting temperature is high enough (above 1450°C) and if the glass has a tendency to phase separation. Depending on the glass system a certain, minimum TiO_2 -concentration is necessary to promote phase separation and subsequent catalyzed bulk crystallization. For instance in the system $Na_2O-TiO_2-SiO_2$ this effective titania-concentration varies between 10–50 mole %, depending on the SiO_2 content. It generally is lowest for the high-silica glasses which require the highest melting temperatures (around 1600°C). Such glasses are darkbrown to violet in color which points to the formation of oxygen vacancies and eventually of Ti^{3+} . The optical absorption spectrum of such glasses shows indeed the characteristic Ti^{3+} -absorption band around 500 m μ .

A much more sensitive method which can be used for Ti^{3+} -concentrations in the order of 1/100 wt% and less is the electron spin resonance spectroscopy. Results of such ESR studies on the formation of Ti^{3+} in

glasses and its dependence on atmosphere, temperature and on chemical composition will be reported in the present paper. It was expected that ESR-spectra would be useful not only for semiquantitative determinations of the Ti^{3+} -concentration but also for allowing conclusions with respect to the oxygen coordination of titanium in glasses using Ti^{3+} as an indicator or probe.

Recent ESR studies on TiO_2 -containing glasses have been reported by Bishay and Gomaa[3] and by Sidorow and Tjulkin[4]. However, these authors investigated centers in such glasses which were generated by gamma irradiation, and they did not report any ESR-spectra of non-irradiated glasses. In departure from earlier ESR-spectra reported for titania-containing glasses[5,8] the above authors attributed the resonance line with $g = 2.01$ to trivalent titanium. Karupetyan *et al.*[6], however, found the same resonance in TiO_2 -free glasses of the system $Na_2O-Al_2O_3-SiO_2$ after gamma irradiation. Silsbee[7] suggested that this resonance which he found in irradiated quartz should be due to an unpaired electron in a non-bonding orbital on silicon. Yafaev and Yablokov[5] who investigated a number of titania-containing silicate glasses observed resonances in the ESR spectra with g varying from 1.922–1.930. They assume that this

resonance is due to Ti^{3+} in octahedral coordination with varying degrees of distortion. The same resonance with $g = 1.94$ was found also by Garif'yanov[8] in a titanium-containing Mg-Al-silicate glass.

Besides titanium other transition elements have been also incorporated into glasses and studied by ESR. The results of Castner *et al.*[9], Kurkjian and Sigety[10] and of Hirayama *et al.*[11] who reported ESR-spectra of Fe-containing glasses were of interest for the present work. All of the sodiumtitanium silicate glasses used for the present study contained iron as impurity in the order of wt%. Kurkjian and Sigety[10] suggested that the resonance with $g = 4.3$ can result from Fe^{2+} either in distorted tetrahedral or octahedral coordination, whereas the appearance of the $g = 2$ resonance is related to the concentration of Fe^{3+} and may be caused by Fe^{3+} - Fe^{3+} coupling in the glass at higher concentrations.

2. EXPERIMENTAL PROCEDURE

2.1 Sample preparation

The glasses investigated were prepared from analytical grade Na_2CO_3 , TiO_2 and Dorentupper quartz sand. Melting was carried out in Pt-Rh crucibles (100 ml) under oxidizing conditions at 1450–1550°C (Kanthal Super electric furnace). Only the glass $5Na_2O \cdot 10TiO_2 \cdot 85SiO_2$ (composition in mole per cent) had to be molten in a gas-fired furnace at around 1600°C. Heat treatment of powdered glasses and of bulk samples was carried out in hydrogen, oxygen or vacuum, well below the crystallization temperature of the glasses usually at around 500–550°C for 40 hr. Some glasses were also exposed to neutron radiation in a reactor (flux = 5×10^{18} neutrons/cm²). The glasses were checked for crystallization before and after heat treatment (X-ray, microscope).

For comparison and for a better interpretation of the ESR spectra of glasses several crystalline titanium oxide compounds with known coordination of titanium were also

prepared, e.g. TiO_2 (rutile, anatase, brookite), $MgTi_2O_5$, $MgTiO_3$, Mg_2TiO_4 , $BaTiO_3$, Ba_2TiO_4 , La_2TiO_5 , $ZrTiO_4$, $Na_2Ti_3O_7$, Ga_2TiO_5 , $Y_2Ti_2O_7$ etc. These compounds were synthesized from analytical grade materials by solid state reactions (pressed and sintered pellets, about 20 mm in dia.) in oxidizing atmosphere. Depending on the compound to be synthesized the reaction temperature varied from 1000°C (for the alkali titanates) to 1550°C (Mg-Ti-oxides). The reaction products were checked for purity by X-rays (Gunier powder camera, CuK_{α} -radiation, long exposure). In order to transform a small amount of titanium from the 4-valent to the 3-valent state, the samples were heat treated in hydrogen at 550 or 650°C for 20 hr. The X-ray patterns did not change after such low-temperature heat treatment. Of course the X-ray method is not sensitive enough to detect crystalline phases with a concentration of less than 1–2 wt%. It is reasonable however to assume that the oxygen coordination of titanium is not affected at these low temperatures.

2.2 ESR-measurements

Bulk samples and powdered samples (grain size 120–160 μ) were used. The EPR-measurements were carried out with a VARIAN Spectrometer E 3 at room temperature and in most cases also at 77°K. The microwave frequency range was about 9.3 GHz (X-band). For field calibration, standards of Mn^{2+} in SrO, or Mn^{2+} in ZnS, or a solution containing VO^{2+} were recorded simultaneously with the Ti^{3+} -resonance.

3. RESULTS AND DISCUSSION

3.1 EPR-spectra of untreated glasses of the system Na_2O - TiO_2 - SiO_2

Glasses molten in air at 1500°C were yellow, brown or violet colored, depending on composition. The ESR-spectra of such glasses showed a number of resonances whose intensity and position also varied with the chemical composition.

In a previous investigation on the system $\text{Na}_2\text{O}-\text{TiO}_2-\text{SiO}_2$ [1, 2] three main regions were established where the corresponding glasses show quite different crystallization behavior (Fig. 1).

(1) Glasses in region *A* are obviously homogeneous and only show surface crystallization upon heat treatment.

(2) Submicroscopic phase separation com-

bined with a characteristic primary crystallization was observed for heat-treated glasses of region *B*.

(3) Glasses of region *C* showed glass in glass separation, however no primary crystallization upon heat treatment was observed. These three regions hold also for the ESR-spectra of the corresponding glasses. Figure 2 shows the ESR-spectrum of a typical re-

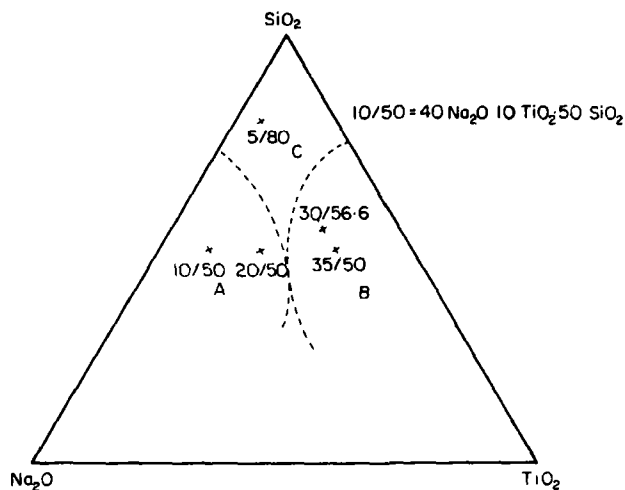


Fig. 1 Glass regions with different crystallization behavior in the system $\text{Na}_2\text{O}-\text{TiO}_2-\text{SiO}_2$.

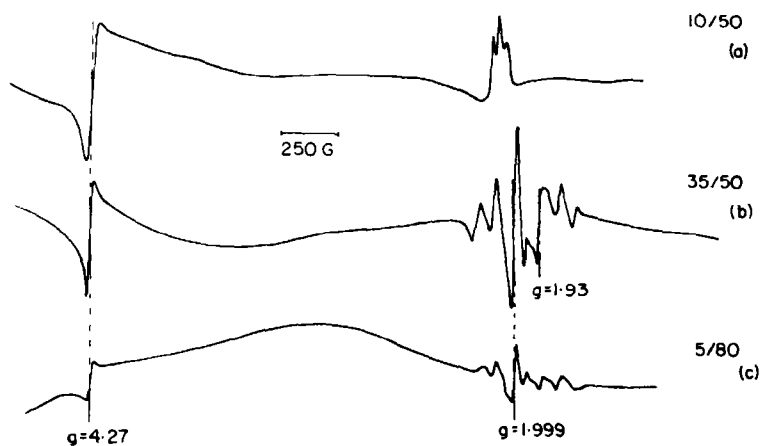


Fig. 2. ESR spectra of glasses from regions (a), (b) and (c) (melted in oxidizing atmosphere at $1450-1500^\circ\text{C}$). Numbers refer to molar ratio $\text{TiO}_2/\text{SiO}_2$.

representative glass for each region. Glasses within the same region give the same resonances, only their intensity varies slightly with the chemical composition. A discontinuous change is found, however, when going from one region to the other.

All three spectra of Fig. 2 have one resonance in common with $g = 4.27$. According to the literature [9–11] this resonance is characteristic for Fe^{3+} . Iron is present as impurity in the starting materials.

Samples of regions *B* and *C* showed another resonance at $g = 1.999$ with a superimposed hyperfine structure of four lines (Fig. 2(b) and 2(c)). This resonance could be due to defects (e.g. oxygen defects) which are created at phase boundaries, because it is found only in glasses which show phase separation. According to Weeks and Bray [12] such defects should give rise to resonances with g -values around 2. Glasses of region *A* showed a resonance with $g = 2$ which was found also in other ternary silicate glasses, e.g. of the system $\text{TiO}_2\text{--CeO}_2\text{--SiO}_2$. The shape of this resonance indicates a strong anisotropy of the g -tensor, that means low symmetry of the crystal field (Fig. 2(a)).

Glasses of region *B* show an additional resonance with $g = 1.93$ which must be assigned to trivalent titanium. This resonance was strongest in glass samples of composition $15\text{Na}_2\text{O} \cdot 35\text{TiO}_2 \cdot 50\text{SiO}_2$ (mole per cent). Glasses of region *B* show crystallization of a characteristic primary phase which contains Ti^{3+} . Therefore it is reasonable to assume that the untreated glass also contains very small regions which are rich in Ti^{3+} . This would be in agreement with previous results [1] obtained by electron microscopy on glasses of similar composition.

3.2 ESR-spectra of glasses heat treated in oxidizing atmosphere

The glass samples discussed in the foregoing section were heated at 500°C in oxygen for 24 hr. that is, below their crystallization temperature. As expected all samples showed a slight increase of the Fe^{3+} resonance. The resonance with $g = 2$ which was found only in glasses of region *A* is now observed in all oxidized glasses (Fig. 3(a), (b)). The Ti^{3+} -resonance and the resonance with $g = 1.999$ including the hyperfine structure have disappeared. It should be emphasized that

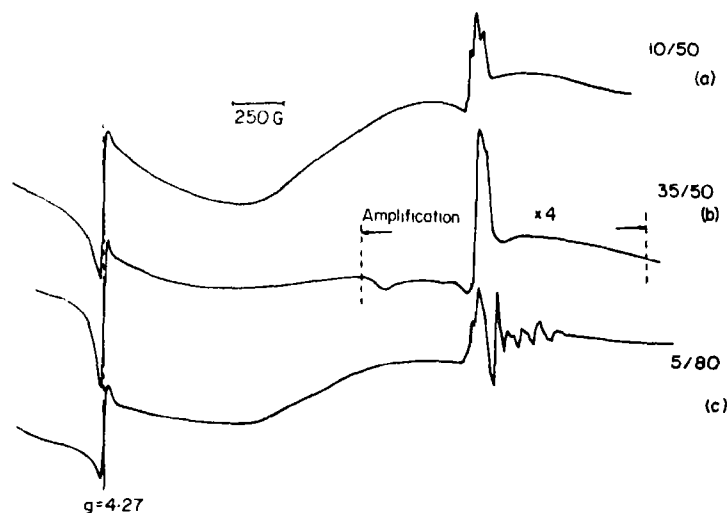


Fig. 3. ESR spectra of glasses after heat treatment in oxygen, 500°C , 24 hr. Numbers refer to molar ratio $\text{TiO}_2/\text{SiO}_2$.

the resonance with $g = 2$ is found only in powdered glass samples (grain size $60\text{--}120\ \mu$). Bulk samples are similarly decolorized upon oxidizing heat treatment, the Ti^{3+} also disappears but their ESR-spectrum is identical to that shown in Fig. 2(c) and not related to the ESR-spectra shown in Fig. 3(a) and 3(b). This points to surface effects, e.g. the powdered samples could bind oxygen atoms and thereby form paramagnetic centers on the surface. Iyengar *et al.*[13] observed a resonance with two satellites at $g = 2$ in rutile which they assigned to a O_2^{+} -center. The resonance shown in Figs. 3(a) and 3(b) could perhaps be due to oxygen molecules which are bound to surface defects. The resonance with $g = 2$ was observed in all powdered glasses of the system including those of region C. These glasses retain the resonance at $g = 1.999$ also after oxidizing heat treatment, which is now superimposed on the new resonance with $g = 2.0$. (Fig. 3(b)).

3.3 ESR-spectra of glasses heat treated in reducing atmosphere

Originally yellow, brown or violet glasses became colorless after heat treatment in oxygen. Such glasses can be colored again by heating in hydrogen for 24 hr at 500°C . The ESR spectra of all these colored glasses now show a strong resonance with g between $1.925\text{--}1.940$ which is attributed to the presence of Ti^{3+} (Fig. 4). The Ti^{3+} -resonance was

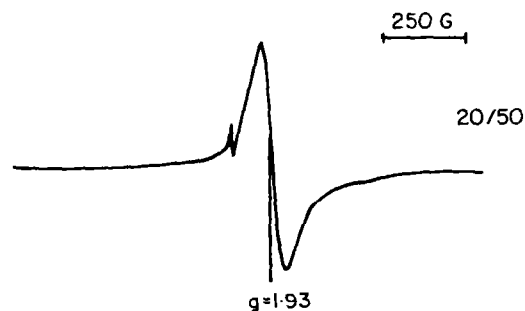


Fig. 4. ESR spectrum of a glass $30\text{Na}_2\text{O} \cdot 50\text{SiO}_2$ after heat treatment in hydrogen, 500°C , 20 hr.

observed in glasses all over the system after such reducing treatment, however its intensity is strongest within the region B (phase separation and primary crystallization). The maximum Ti^{3+} -concentration was centered around a glass of composition $15\text{Na}_2\text{O} \cdot 35\text{TiO}_2 \cdot 50\text{SiO}_2$. The shape of the resonance of glasses within this region indicates a slight anisotropy, whereas the resonance of glasses outside region B points to a strongly isotropic g -tensor. Not only the shape but also the position of g changes discontinuously when crossing from one region into the other.

Glasses of region A show a shift of the g -values from 1.930 to 1.935 with increasing SiO_2 -concentration. For glasses of region C and of region B the Ti^{3+} -resonance was found in the order $1.925\text{--}1.930$, and $1.933\text{--}1.941$ respectively.

The center which is responsible for this resonance is generated by heat treatment in hydrogen and disappears after corresponding treatment in oxygen. Probably hydrogen diffuses into the glass and breaks up an oxygen bridge on the titanium. It is assumed that the center which causes the resonance with $g = 1.925\text{--}1.940$ looks like Fig. 5. The other possibility for generation of a center would be the diffusion of oxygen leaving vacancies in the place of bridging oxygens. This is very unlikely to happen however at these low temperatures, as could be proved also by experiments in vacuum which are described in the following section.

In addition to the Ti^{3+} -resonance, all samples showed a very sharp resonance with $g = 1.999$ (width about $5\ \text{G}$). Its inten-

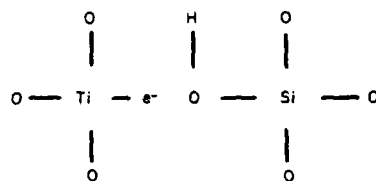


Fig. 5. Ti^{3+} -center generated by heat treatment in hydrogen.

sity is highest for glasses of region A. The g value of this resonance corresponds exactly to that of the resonance shown in Fig. 2(b) and 2(c), however it is not sure whether it belongs to the same center. The exceptionally sharp resonance could be generated either by reduction of cations or by incorporation of H into the glass structure.

3.4 Relations between ESR-absorption and optical absorption in the visible and I.R.

The results derived from experiments in hydrogen suggest that the Ti^{3+} -center is generated by bonding of hydrogen to one of the coordinating oxygens. Therefore it was of interest to investigate any relation between the ESR-absorption, the optical absorption at around $500\text{ m}\mu$ and the i.r. absorption in the region of the OH-band. For such experiments small polished glass plates were used (glass composition $15Na_2O \cdot 55SiO_2 \cdot 30TiO_2$), which were heat treated before in hydrogen (500°C , 72 hr). These 'reduced' samples were oxidized (decolorized) gradually by stepwise heat-treatment in oxygen, and the various spectra were recorded after each step.

A qualitative relationship between color of the samples and their ESR-spectra was obvious already from the experiments described in the foregoing section. Measurements of the OH band (at around $2.8\text{ }\mu$)

showed that the OH-concentration decreases very little during the decolorization process. Most of the OH (approx. 98 per cent) cannot be removed by heat treatment in oxygen and probably is bound to silicon. Only a small concentration of the hydrogen atoms which are bound to bridging oxygens of titanium can diffuse. Due to the high OH-background of the glass it was necessary to carry out difference measurements, in which the samples were measured against a completely decolorized sample of the same composition.

The optical absorption was measured by means of a photometer with a suitable interference filter; the transmission of identical sample areas was recorded.

ESR-curves were integrated twice for evaluation, taking the integral as a measure for the concentration of the centers.

Fig. 6(a) corresponds to a plot of the ESR-absorption vs. optical absorption. The measured values lie on a straight line through the origin. This is a strong indication that the d -electron of the Ti^{3+} -center (which is in a t_{2g} orbital) is responsible for the ESR-absorption and for the optical absorption.

The relationship between the OH-concentration and the ESR-absorption is approximately a linear one, the OH-concentration increases with increasing number of resonance centers (Fig. 6(b)). This result is another

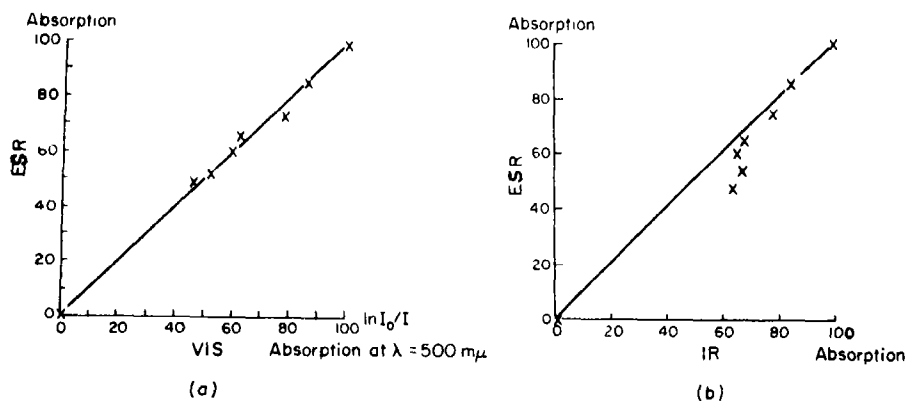


Fig. 6. Relation between ESR-absorption (Ti^{3+} -resonance) and optical absorption in the visible (Ti^{3+}) and in the infrared (OH⁻)

indication that hydrogen is directly involved in the reduction of titanium as it is shown by Fig. 5. For the difference measurements the OH-concentration was assumed to be 0 for the completely oxidized sample and 100 for the completely reduced sample.

3.5 Experiments in vacuum

Powdered samples were strongly colored (brown to violet) after heat treatment in hydrogen. Heating such glasses at 500–600°C for 20 hr in vacuum (about 10^{-5} torr) caused complete decolorization and disappearance of the Ti^{3+} -resonance at $g = 1.93$. This proved that the Ti^{3+} -center is connected with the incorporation of OH into the glass. When heated in vacuum such glasses give off hydrogen with simultaneous reoxidation of titanium from the 3-valent to the 4-valent state. The degree of bleaching depends on the grain size as one would expect it for a diffusion process. Bulk samples are decolorized very slowly and not completely under such conditions in contrast to powdered samples. On the other hand, when a completely oxidized, Ti^{3+} -free bulk sample was heated up again in vacuum it became gradually brownish colored with simultaneous appearance and increase of the Ti^{3+} -resonance. This effect was not found for powdered samples. Probably the hydrogen which is present in all glasses as OH can diffuse more easily to a nearby titanium ion than to the surface in bulk samples, because of the long diffusion path and the low temperature. Such diffusion obviously only occurs in vacuum but not in oxygen.

It was shown that oxidizing heat treatment generates a resonance with $g = 2.0$ in all glasses of the system (Fig. 3(a)). This resonance was not observed in any of the glasses after heating in vacuum. This is in agreement with the assumption that the resonance with $g = 2$ is due to surface effects, e.g. due to O_2^{+} -centers which originate from O_2 -molecules bound to the surface.

3.6 ESR-spectra of samples after irradiation in a reactor

Binary and ternary compositions of the system $\text{Na}_2\text{O}-\text{TiO}_2-\text{SiO}_2$ were irradiated in a reactor, that means exposed to radiation which consists mainly of slow neutrons (flux $10^{18}/\text{cm}^2$), but also of fast neutrons and γ -rays. The aim of these investigations was to induce Ti^{3+} -centers and other centers and to compare these to identical samples heat treated in hydrogen etc. None of the above bulk samples showed any resonances in the ESR spectra before neutron irradiation (TiO_2 -containing samples were oxidized before). After irradiation some characteristic resonances were found. One would expect that such irradiation should generate a number of defects in vitreous or crystalline oxides), O'-centers, etc. Resonances due to such defects and centers in oxide glasses have been observed by several authors and have been investigated in detail by Weeks and Bray[12]. They conclude that the g -values of such centers should be close to the value of the free electron $g_{el} = 2.0023$. The g -values which they measured for various oxide compounds and glasses after irradiation with neutrons or γ -rays were between 2.03 and 1.99. The samples listed in Table I also show resonances of this type, with g -values varying in this range. The observed resonances obviously consist of several, superimposed resonances (Fig. 7). This indicates that probably several of the above-mentioned defects are present. The resonance around $g = 2$ found in the irradiated samples should also be identical to the one observed by Sidorow and Tjulkin[4] which they erroneously assigned to the Ti^{3+} -center. As Table I shows, this resonance is present also in Na-disilicate glasses. The titania-containing samples showed another resonance with $g \sim 1.93-1.94$ which should be due to the presence of Ti^{3+} . Irradiation of the samples probably induces an oxygen defect at the Ti^{4+} and at the same time one O' is shifted to an 'interstitial lattice position' (Fig. 8). The

Table 1. ESR-resonance lines of various compounds after irradiation in a reactor

Composition (moles)				g-values	
(a)	28.33 Na ₂ O	56.67 SiO ₂	15 TiO ₂	(glass)	2.02 1.942
(b)	15 Na ₂ O	55 SiO ₂	30 TiO ₂	(glass)	1.997 1.936
(c)		92 SiO ₂	8 TiO ₂	(glass)	1.994 1.92
(d)	33.33 Na ₂ O	66.67 SiO ₂		(glass)	2.04
(e)	2 Na ₂ O	6 TiO ₂		(cryst.)	1.998 1.925

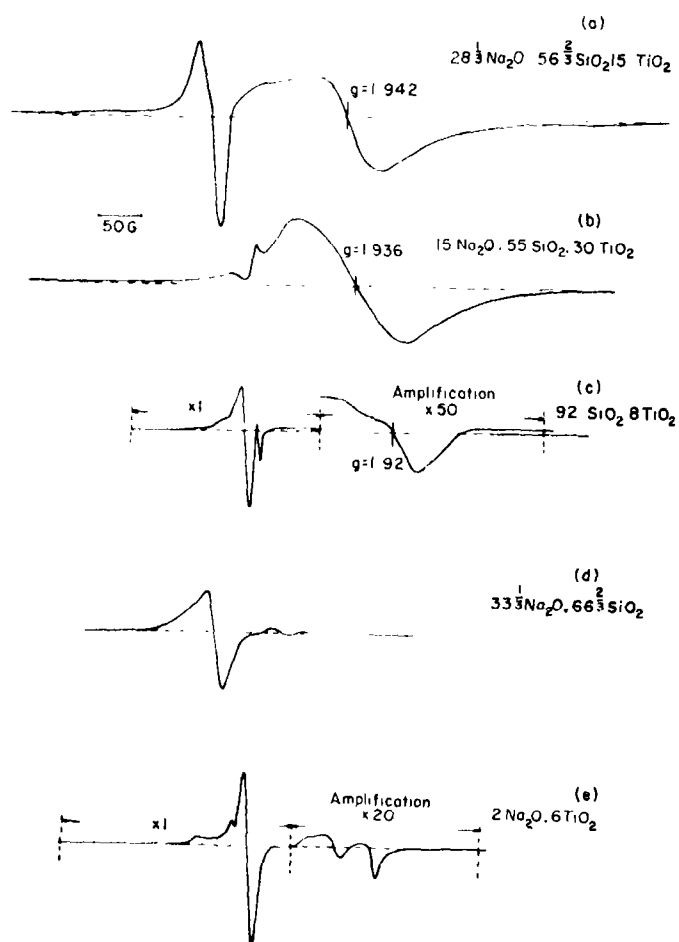
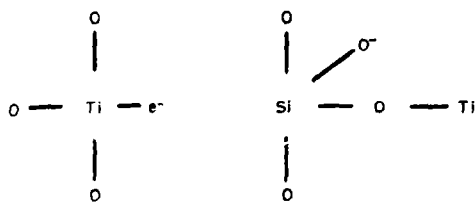


Fig. 7. ESR spectra of neutron irradiated samples.

Fig. 8. Ti^{3+} -center induced by neutron irradiation.

latter then causes the resonance with $g \sim 2$. The Ti^{3+} -resonance observed after irradiation occurs practically at the same position as the one found in glasses heat treated in hydrogen (e.g. for glass *b* of Table 1, $g = 1.936$ compared to $g = 1.933$). The shape of the resonance in the case of the O' -vacancy points to a stronger anisotropy of the g -tensor, whereas only slight anisotropy is found in the case of the OH-center formed by reduction in H_2 (see Figs. 7(b) and 7(c), Fig. 4). In the first case the bridging oxygen is missing (Fig. 8), in the second case it is compensated by a proton (Fig. 5). This results in a much stronger, axial distortion of the crystal field for the O' -vacancy, and leads to only slight deviation from cubic symmetry when an OH-center is formed.

3.7 ESR-study of crystalline titanium oxide compounds

ESR-spectra of various, crystalline compounds have been recorded for comparison. Oxide compounds with known coordination of titanium and if possible also with known Ti-O distances were prepared for these investigations. It was anticipated that comparison between the position and the shape of the Ti^{3+} -resonance in glass to that in crystalline samples would show some dependence of the resonance curve on the crystal field symmetry.

Most samples were used in powdered form. In these cases the symmetry of the crystal field can be derived from the shape of the resonance by the method of Kneubühl[14] and of Ibers and Swalen[15]. The TiO_2 -modifications rutile, anatase and brookite were available in form of small single crystals. All these modifications show octahedral oxygen coordination around titanium which is somewhat distorted, especially in brookite. The average Ti-O distance is about the same, around 1.946–1.960 Å. Figure 9 shows the ESR spectrum of brookite and anatase after reduction at 600°C in H_2 . The g -value of the Ti^{3+} -resonance is only slightly higher than

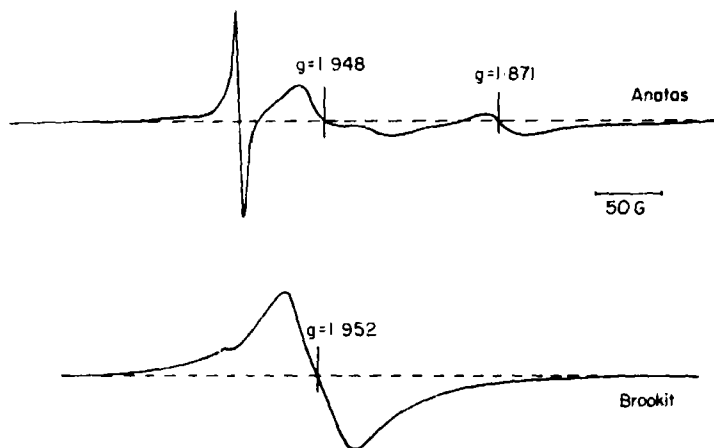


Fig. 9. ESR spectra of anatase and brookite after heat treatment in hydrogen, 600°C, 20 hr.

that found for glasses, e.g. around 1.95. Polycrystalline rutile showed a resonance at $g = 1.945$.

Most of the Ti-containing oxide samples used in this study also contain titanium in 6-fold oxygen coordination. These are listed in Table 2 together with their Ti-O distances and the measured g -values (value where $d\phi/dH = 0$). The ESR-spectra are shown in Fig. 10.

Comparison of the various resonance curves indicates that the octahedral oxygen coordination of Ti^{3+} is more or less distorted. The resonance in Ga_2TiO_5 points to an isotropic g -tensor. Therefore the point symmetry of Ti^{3+} should have only slight, axial distortion. Lowering of symmetry is caused already by bonding of hydrogen to one of the oxygens. Axial symmetry is probably present in $K_2Al_2Ti_6O_{16}$, $NaTi_2Al_5O_{12}$, Mg_2TiO_4 and $MgTiO_3$ as can be seen from the corresponding resonance curves. Ti-O distances are known for $NaTi_2Al_5O_{12}$, the titanium is shifted out of the basal plane in the direction to one of the oxygens at the apex of the octahedron. The tetragonal point symmetry however is still maintained, in accordance with the features characteristic for axial symmetry which are found in the resonance curve. For the other compounds the point symmetry is probably orthorhombic or lower symmetric. In $ThTi_2O_6$ titanium obviously has monoclinic point symmetry. The resonance curve for

$Y_2Ti_2O_7$ shows the features of orthorhombic symmetry. A special case is $MgTi_2O_5$, where titanium occupies two different sites in a so-called pseudo-brookite structure. One titanium shows fairly octahedral oxygen coordination whereas the other titanium has a strongly distorted 6-fold oxygen coordination with 2 oxygens farther away. The resonance spectrum can be interpreted in agreement with this as a superposition of two resonances with isotropic and with anisotropic g -tensor.

When discussing the point symmetry of Ti^{3+} it is important to recall that the Ti^{3+} -center is generated by bonding of hydrogen to one of the oxygens of the coordination octahedron. Therefore there are several, non-equivalent positions available for OH depending on the kind of distortion of the Ti-oxygen octahedron. In the case of axial distortion, the axial point symmetry will be maintained after incorporation of H only if the OH-group is situated on the apex of the octahedron and not in the basal plane. This seems to be true for the compounds $K_2Al_2Ti_6O_{16}$ and especially for $NaTi_2Al_5O_{12}$. One could assume that the formation of the OH group takes place preferably at that oxygen which has the weakest bond to titanium that means where the distance Ti-O is largest. Otherwise it would not be possible to explain the typical axial symmetry as it is found in the ESR-spectrum.

Table 2. Titanium oxide compounds with 6-fold coordinated titanium

(Ti-O distances)		
(1)	$K_2Al_2Ti_6O_{16}$	$g = 1.968$ (77°K)
(2)	$NaTi_2Al_5O_{12}$ ($2 \times 1.952, 2 \times 1.973, 2.167, 1.843$ Å)	$g = 1.961$ (77°K)
(3)	$ThTi_2O_6$ ($2 \times 1.83, 2 \times 1.94, 2.06, 2.20$ Å)	$g = 1.931$ (77°K)
(4)	Mg_2TiO_4 (1.944 Å)	$g = 1.96$ (77°K)
(5)	Ga_2TiO_5	$g = 1.930$ (77°K)
(6)	$Y_2Ti_2O_7$	$g = 1.910$ (77°K)
(7)	$MgTi_2O_5$	$g = 1.950$ (77°K)
(8)	$MgTiO_3$	$g = 1.943$ (77°K)

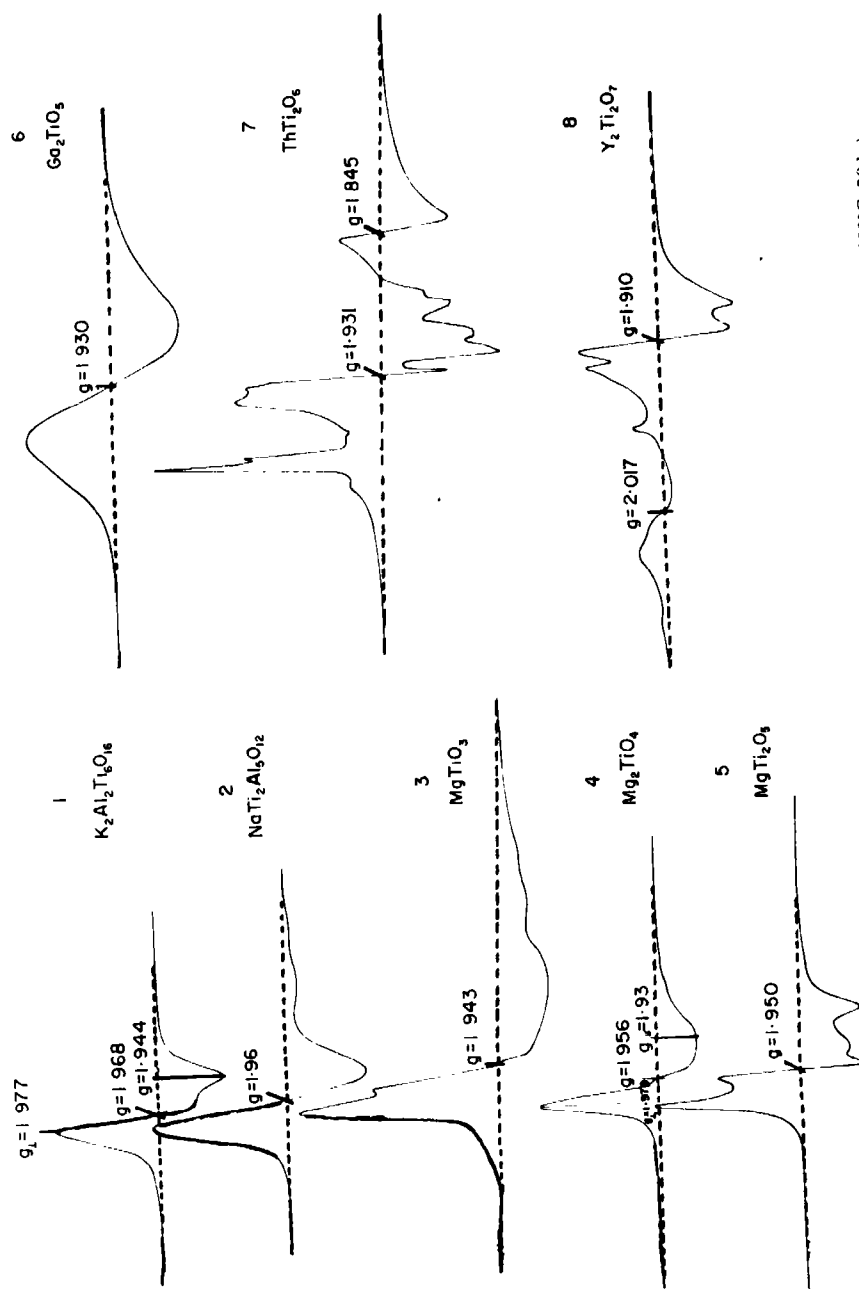


Fig 10. ESR spectra of oxide compounds with 6-fold coordinated titanium (heat treated in hydrogen, 650–900°C., 20 hr).

Besides 6-fold oxygen coordination, also lower oxygen coordination is known for titanium. Two such compounds are listed in Table 3, and ESR-spectra are shown in Fig. 2.

The point symmetry of titanium in these compounds is low in agreement with the shape of the resonance curves shown in Fig. 11. These examples also show that it is not possible to derive coordination numbers from the position and shape of the resonance. The point symmetry of the center is the main factor which determines the shape of the resonance whereas the intensity of the interaction between the paramagnetic electron and the crystal field is responsible for the position of the resonance.

4. SUMMARY AND CONCLUSIONS

ESR-study on glasses of the system $\text{Na}_2\text{O}-\text{TiO}_2-\text{SiO}_2$ showed the following results

(1) Trivalent titanium is formed under oxidizing melting conditions above 1450°C in glass compositions which are inside the

region of immiscibility (area (b) in Fig. 1). Glasses with the strongest tendency to phase separation have the highest Ti^{3+} -concentrations. This is probably true also for other glassforming systems which contain TiO_2 .

(2) Oxidizing heat treatment (500°C) below the crystallization temperature causes disappearance of the Ti^{3+} resonance at $g = 1.93$.

(3) Heat treatment in hydrogen (at 500°C) leads to formation of Ti^{3+} in all glasses, and to a strong increase of the Ti^{3+} concentration in glasses of region (b), respectively. The shape and the position of the Ti^{3+} -resonance is somewhat different for regions (a), (b) and (c) of the system. This points to differences in the oxygen surrounding of titanium. The Fe^{3+} -resonance at $g = 4.27$ is no longer present.

(4) Different behaviour was found for glasses when heated in vacuum ($500-600^\circ\text{C}$): oxidized bulk samples showed formation of

Table 3 Titanium oxide compounds with 5-fold and 4 fold oxygen coordination

La_2TiO_5 (5 fold oxygen coordination)	$g = 1.881$ (300°K)
TiO 1.74, 1.83, 1.92, 2 + 2.03 Å	
Ba_2TiO_4 (4 fold oxygen coordination)	$g = 1.977$ (77°K)
TiO 1.63, 1.64, 1.75, 1.82 Å	$g = 1.972$ (300°K)

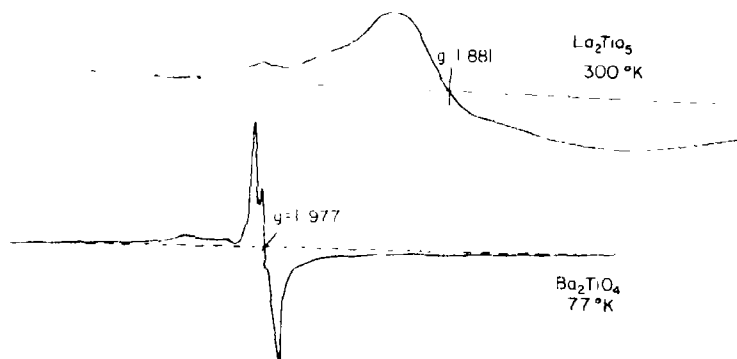


Fig. 11 ESR spectra of oxide compounds with 5- and 4-fold coordinated titanium (heat treated in hydrogen 900°C , 20 hr)

trivalent titanium, whereas reduced powder samples became oxidized.

(5) A linear relationship was found between the optical absorption of Ti^{3+} at $500 m\mu$ and the ESR-resonance at $g \sim 1.93$, and also between the OH' -absorption band at around 2.8μ and the Ti^{3+} -resonance at $g \sim 1.93$. These results indicate that hydrogen is directly involved in the reduction of titanium.

(6) Experiments with neutron irradiation proved that under these conditions a Ti^{3+} -center is formed in glasses and in crystalline compounds. The resonance is observed practically at the same position as in the case of samples reduced in hydrogen. However, the shape of the resonance is different and points to a stronger anisotropy of the g -tensor for the irradiated samples. Another resonance at around $g = 2$ which was found in all samples after irradiation is probably due to several defects such as oxygen vacancies and O' centers.

No attempts were made to determine the Ti^{3+} -concentration quantitatively by chemical analysis, because iron was present as impurity in all samples in about the same concentration. Suitable reference samples containing Ti^{3+} for evaluation of ESR-spectra were not available.

The ESR-spectra of various oxide compounds which contain titanium in 4-, 5-, and 6-fold oxygen coordination proved that it is not possible to derive coordination numbers

for titanium directly from the position and from the shape of the Ti^{3+} -resonance.

Acknowledgements—The authors wish to thank Dr. G. Luckhurst and Dr. J. Ockwell for helpful discussions and the Varian Research Laboratory, Zurich, for generously provided the facilities for the ESR measurements. The technical assistance of W. Hirsiger in all phases of the experimental work is gratefully acknowledged. This study was supported by Owens-Illinois Inc., Toledo, Ohio.

REFERENCES

1. BAYER G., FLOERKE O. W., HOFFMANN W. and SCHEEL H. J., *Glastech. Ber.* **39**, 242 (1966).
2. BAYER G. and HOFFMANN W., *Glass Techn.* **7**, 94 (1966).
3. BISHAY A. and GOMAA I., *Physics Chem Glasses* **9**, 193 (1968).
4. SIDOROV I. A. and TJULKIN W. A., *Neorgan Materialy* **4**, 578 (1968).
5. YAFAEV N. R. and YABLOKOV Y. V., *Soviet Phys.-solid St.* **4**, 1123 (1963).
6. KARUPETIAN G. O., KONDRATEV Y. N. and YUDIN D. M., *Soviet Phys.-solid St.* **6**, 1219 (1964).
7. SILSBEE R. H., *J. appl. Phys.* **32**, 1459 (1961).
8. GARIF'YANOV N. S. and TOKAREVA L. V., *Soviet Phys.-solid St.* **6**, 1137 (1964).
9. CASNER T., NEWELL G. S., HOITON W. C. and SLICHTER C. P., *J. chem. Phys.* **32**, 668 (1960).
10. KURKJIAN C. R. and SIGETY E. A., *Physics Chem. Glasses* **9**, 73 (1968).
11. HIRAYAMA C., CASTLE J. G. and KURIYAMA M., *Physics Chem. Glasses* **9**, 109 (1968).
12. WEEKS R. A. and BRAY P. J., *J. chem. Phys.* **48**, 5 (1968).
13. IYFNGAR R. D., CODELL M., KARRA J. S. and TURKEVICH J., *Am. chem. Soc.* **88**, 5055 (1966).
14. KNEUBUEHL F. K., *J. chem. Phys.* **33**, 1074 (1960).
15. IBERS J. A. and SWALEN J. D., *Phys. Rev.* **127**, 1914 (1962).

TECHNICAL NOTES

Thermally stimulated currents in Cu_2O

(Received 2 June 1969; in revised form 11 March 1970)

CUPROUS oxide samples were prepared in the way described in the preceding note and annealed under vacuum. The platelets ($4 \times 4 \times 1$ mm) were equipped with guard ring electrodes. They were mounted on a copper block at the end of a cold finger and illuminated with a high pressure mercury lamp. Temperature was detected with a thermocouple directly attached to the guard ring.

The speed of temperature rise β was low enough ($10^{-2} < \beta < 10^{-10}$ /sec) to insure good thermal linearity and homogeneity within the sample assembly.

The thermally stimulated currents (TSC) were measured on a Keithley logarithmic picoammeter. The plot was directly recorded on an *XY* recorder as a function of $10^3/T$ through a function generator adapter. TSC bumps appear clearly in the vicinity of 130°K. Figure 1 gives an example of such a record. Nevertheless it must be noticed that the maximum current was not large enough in comparison with 'dark' current I_0 , so that no information can be given by the slope of the low temperature side of the peak[1]. Then the TSC were analysed using the two independent methods of Haering-Adams[2] and Booth[3] assuming $E_t/kT_m \gg 1$, where E_t is the trap depth and T_m the temperature corresponding to the maximum of the peak.

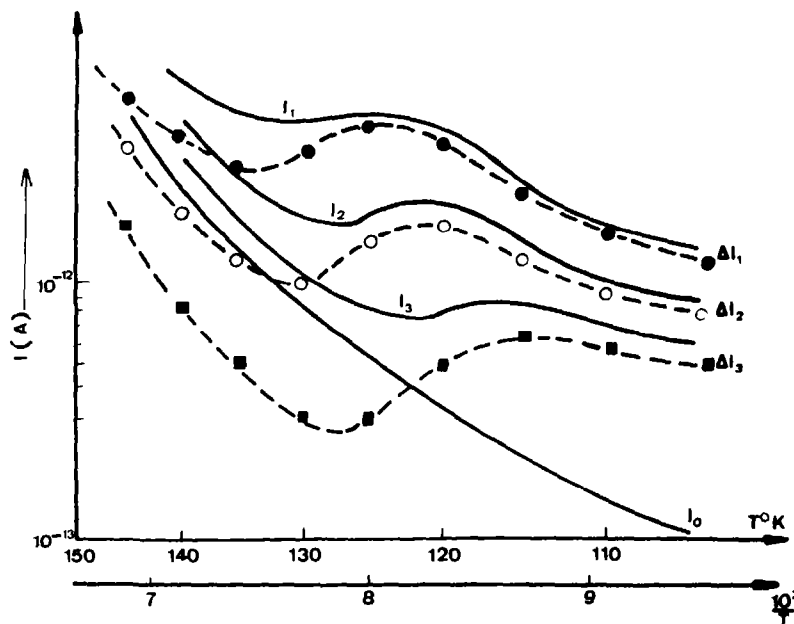


Fig. 1. Thermally stimulated currents; I_1 , I_2 , I_3 refer to the corresponding value of $\beta_1 = 8.6 \cdot 10^{-2}$, $\beta_2 = 3.4 \cdot 10^{-2}$, $\beta_3 = 1.17 \cdot 10^{-2}$ /sec. ΔI_1 , ΔI_2 , ΔI_3 are the deviations of I_1 , I_2 , I_3 with the dark currents I_0 .

Haering-Adams calculation of *TSC* leads to an expression of the maximum conductivity.

$$\sigma_m = \sigma_0 \exp -\frac{E_t}{kT_m}$$

parameter β and in this way is independent of the previous determination. This leads to the relation

$$\exp \frac{E_t}{kT_m} \sim \frac{T_m^2}{\beta}$$

Varying the speed β gives the pairs of σ_m and T_m plotted on Fig. 2 (corresponding values for the sample described in Fig. 1). It is seen that the exponential dependence gives an activation energy $E_t = 0.285$ eV for the trap involved.

Booth's method is similar but includes the

We plotted $\text{Log } T_m^2/\beta$ vs. $10^3/T_m$ (Fig. 2) and determined $E_t = 0.295$ eV in good agreement [4] with the preceding value and in accordance with the first condition $E_t/kT_m \approx 24 \gg 1$.

It must be also noted that the place and the shape of the *TSC* peak is unaffected by varying the initial filling of the trap, for a constant

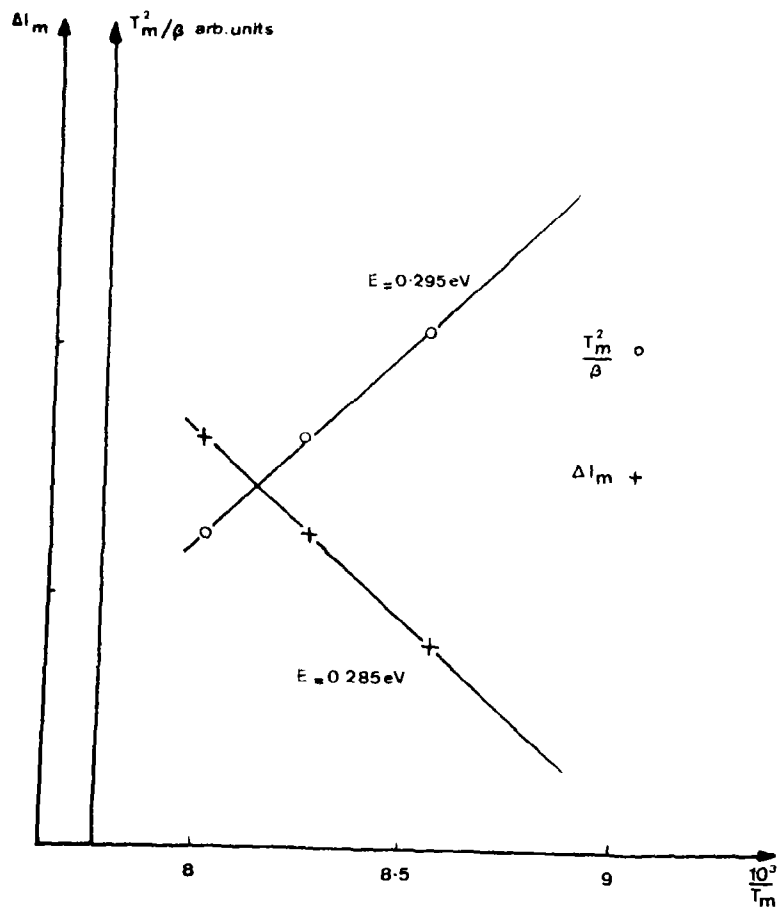


Fig. 2. Determination of the trap depth from Booth's and Haering's plots.

β . This may account for a well defined discrete level.

On the other hand such a trap level can be ascribed to majority carriers (i.e. holes) because reversing the polarity (front electrode being negatively biased) makes the peak disappear.

This observation seems in good accordance with previous work on cuprous oxide that emphasized a hole trap level at 0.3 eV above the valence band[5]. These authors ascribe this trap level to an oxygen vacancy.

J. P. FILLARD
J. GASLOT

Centre d'Etudes d'Electronique des Solides associé au
C.N.R.S.,
Faculté des Sciences de Montpellier, France

REFERENCES

1. GARLICK G. F. J. and GIBSON A. F., *Proc. phys. Soc. Lond.* **A60**, 574 (1948).
2. HAERING R. R., ADAMS E. N., *Phys. Rev.* **117**, 2 (1960).
3. BOOTH A. H., *Can J. Chem.* **32**, 214 (1954).
4. ZIELINGER J. P., ZOUACHI M., CORET A., *J. Phys.* **27**, 166 (1966).
5. O'KEEFE M., MOORE W. J., *J. chem. Phys.* **35**, 1324 (1961).

J. Phys. Chem. Solids Vol. 31, pp. 2141-2145

Electrical conductivity and space charge Cu_2O

(Received 2 June 1969; in revised form 11 March 1970)

CONDUCTIVITY and Hall measurements have been performed on high resistivity Cu_2O samples ($10^{-8} < \sigma_0 < 5 \cdot 10^{-5} \Omega^{-1}$)[1].

Cuprous oxide was epitaxially grown from pure and oriented copper slices[2] and ground down to less than half thickness in order to remove the low defect concentration part of the sample. The conductivity and Hall effect were measured within the temperature range 80–450°K. It was noticed, for both the Hall mobility and the carrier density, a critical

dependence on the thermal history of the sample.

Two types of thermal treatments were selected (1) annealing during a few minutes at $T = 1250^\circ\text{K}$ under vacuum (2) heating two hours at $T = 500^\circ\text{K}$ under vacuum, the sample not being exposed to the air before the electrical measurements were performed.

From the conductivity plot (Fig. 1) it may be noted that annealing enhances the slope and reduces strongly the ambient conductivity σ_0 whereas the outgassing works only in the weak conductivity range. The p type character of the material has been checked with a hot probe test. The activation energy observed 0.25–0.44 eV lies close to a trap level attributed to an oxygen vacancy (see the next paper).

From the mobility plot it can be seen that annealing lowers the mobility and leads to a complex temperature dependence, whereas outgassing leads asymptotically to the previous results of Fortin and Weichmann[3] who show a decreasing dependence of μ_H with increasing T (Fig. 2).

We next used Cu_2O platelets mounted in sandwich cell configuration; the front electrode was a Nesa coated thin glass slide, the back one was painted with silver paste and equipped with a guard ring.

Space charge injection was provided by a light flash creating a sink of electron-hole pairs in the immediate vicinity of the transparent electrode. A bias voltage swept the right polarity carriers and the pulse of SC current associated with the flash was measured on a scope. The operating conditions needed bias voltages such that the transit time ($T_r < 10^{-6}$ sec) was not directly observable. Nevertheless Many's[4] theory on pulsed SCLC implies that initial current I_0 is given by $I_0 \approx \epsilon \mu V^2/d^3$. (Fig. 3) shows a plot of I_0 vs. V for different light levels. By this way we determined the drift mobilities μ_e and μ_h that lie close together and in good agreement with the Hall mobility at room temperature, within experimental errors. SCLC samples were

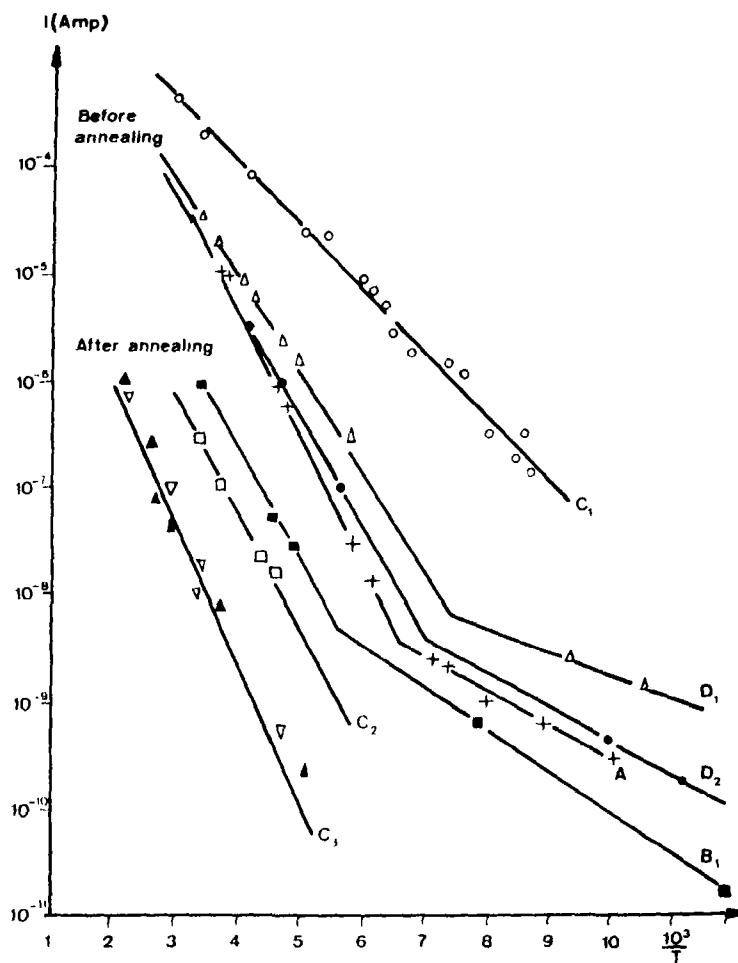


Fig. 1 Conductivity dependance with temperature as a function of thermal history. Sample A, before any heat treatment —○—○—, Sample B, after annealing 1250°K B_1 —■— and out gassing B_2 ——▲—; Sample C: before any heat treatment C_1 —○— (high O_2 pressure during oxidation). After annealing 1250°K C_2 ——□— and out gassing C_3 ——▽—; Sample D, before any heat treatment D_1 ——△— after out gassing D_2 ——●—.

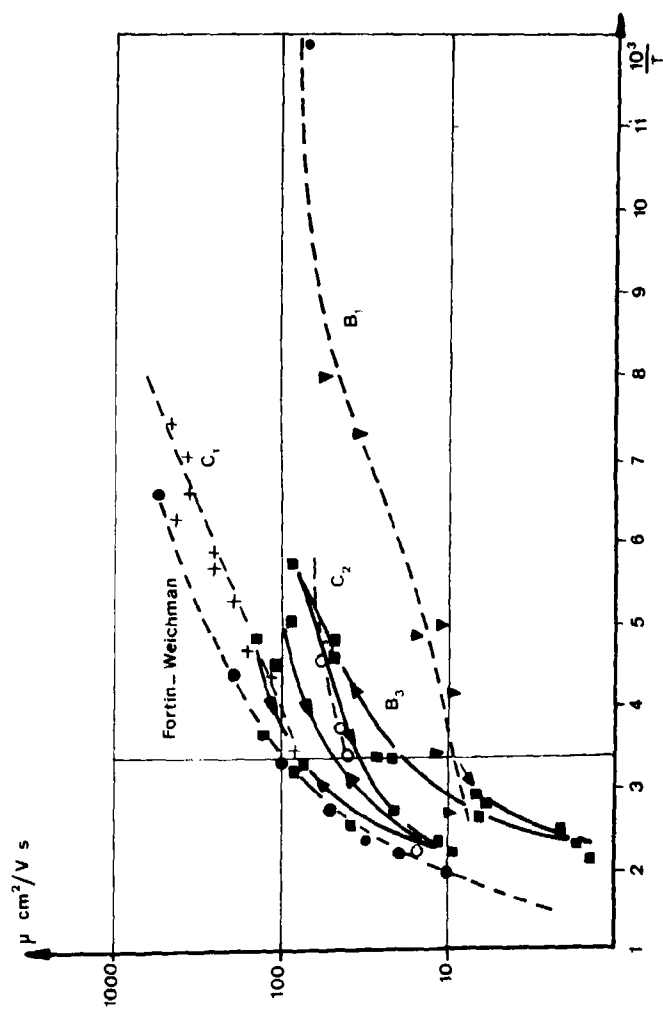


Fig. 2. Hall mobility temperature dependence (the key is the same as for Fig. 1)

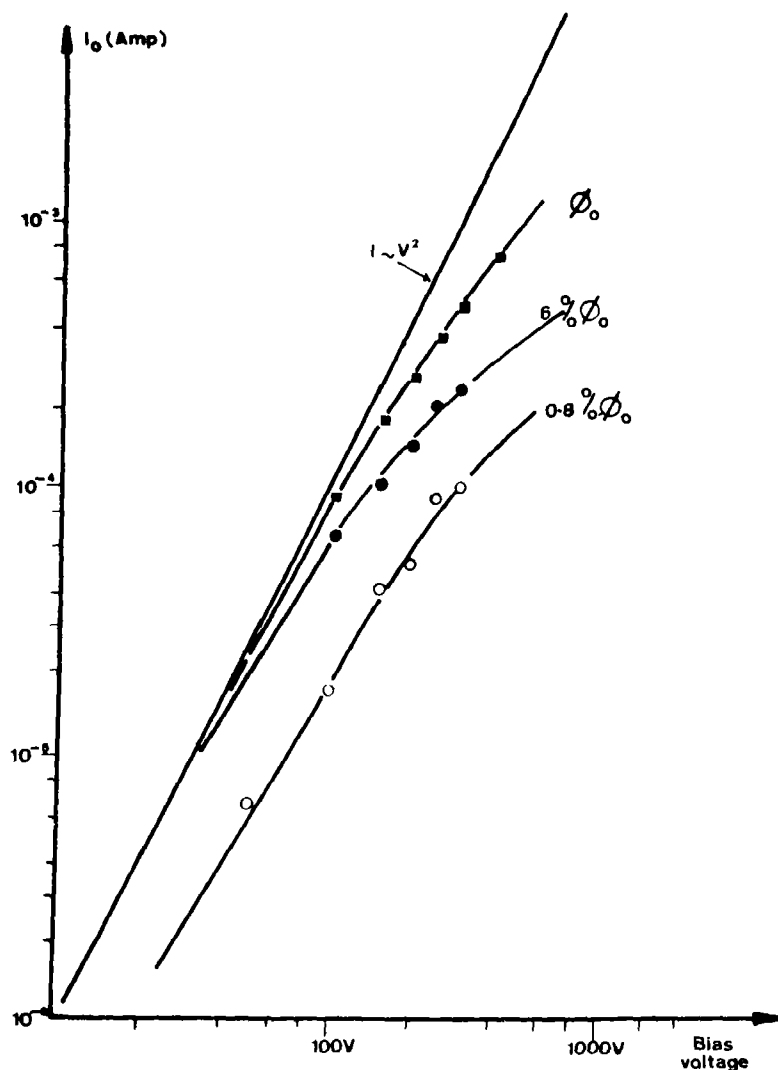


Fig. 3 Initial SC current vs. bias voltage as a function of incident light intensity.

submitted to the same thermal treatment as previously described. The evolution of μ_r and μ_n follows strictly that noted for μ_H . These results shed more light on the discussion of the scattering process as first attempted by Fortin—first of all they confirm that measured mobility refers to bulk properties in such way that surface influence can be eliminated from the discussion; then they

agree with a reproducible temperature dependence after thermal cycling under vacuum. This dependence of μ vs. T does not look so easy to explain unless it is done in the way suggested by Elliott[5] and Fortin involving a splitting of both conduction and valence band. So we tried to select either the injection of heavy or of light carriers by varying the impinging wavelength, but this

attempt was unsuccessful. Another interpretation has been carried out by Young and Schwartz[6] that emphasized a hopping model. The present agreement of drift and Hall mobilities added to the inverse dependence of μ vs. T leads to the opinion that such a hopping model is very unlikely.

Département de Physique,
Université de Sherbrooke,
P.Q., Canada

J. P. CHARLES

J. P. FILLARD

Centre d'Etudes d'Electronique des Solides,
Associé au C.N.R.S.,
Faculté des Sciences,
Montpellier,
France

REFERENCES

1. CHARLES J. P., Thèse de spécialité, Montpellier (1967).
2. BOUGNOT J., Thèse, Lyon (1963).
3. FORTIN E. and WEICHMAN F. L., *Can. J. Phys.* **44**, 1551 (1966).
4. MANY A. and RAKAVY G., *Phys. Rev.* **126**, 1980 (1962).
5. ELLIOTT R. J., *Phys. Rev.* **124**, 340 (1961).
6. YOUNG A. P. and SCHWARTZ C. M., *J. Phys. Chem. Solids* **30**, 249 (1969).

J. Phys. Chem. Solids Vol. 31, pp. 2145-2148.

Transformations of red amorphous and monoclinic selenium

(Received 22 September; in revised form 16 February 1970)

1. INTRODUCTION

THE STRUCTURE of red amorphous selenium and its transformations are not well known. Mondain-Monval[1] and Richter *et al.*[2] assumed that red amorphous and vitreous selenium which has been subject to many investigations[3,4] differ from each other only by the state of their aggregation. Based upon combustion experiments Gattow[5], however, calculated different heats for the hypothetical transformations red amorphous-trigonal and vitreous-trigonal at 25°C. His results proved to be independent of the grain

size, which means that the bulk properties of the two modifications are different.

It is known that red amorphous selenium darkens in colour at temperatures above 30°C, finally becoming black. In this temperature range it is supposed to be subject to configurational changes[6]. The present paper gives details on the transformations of red amorphous selenium near 30°C.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUES

Red amorphous selenium is usually prepared by reduction of selenium acid. It is supposed, however, that impurity atoms like oxygen e.g. which might be incorporated in the selenium molecules during the chemical preparation will influence the physical properties of the pure substance. Another preparation method is the quenching of selenium vapour. At 1000°C selenium is known to consist almost completely of Se_2 molecules[7]. In order to avoid memory effects[8] we passed vapour of 99.999% selenium (American Smelting and Refining Company) through a quartz labyrinth of 1000°C directly into the vapour of boiling nitrogen where it condenses to the red amorphous selenium. The nitrogen was kept extremely free from oxygen (less than 3 ppm), because selenium vapour is oxidized to SeO_2 at elevated temperatures. The oxygen content of the samples was determined by a radiochemical method[9] and did not exceed 10 ppm. Any influence of nitrogen on the physical properties of selenium has never been observed.

The specimens taken for analysis were either as prepared or kept at various temperatures around 30°C in the dark and in an atmosphere of pure argon (purity 99.999 per cent). The storage temperatures were 17.0, 19.7, 23.2, 25.8, 28.4, 31.0, 34.8 and 40.0°C. The storage times extended to one year.

The samples were investigated by differential scanning calorimetry and X-ray analysis. In the differential scanning calorimeter (DSC-1B, Perkin-Elmer) the sample and an

inert reference probe are heated at a constant rate. Individual heat flow rates maintain the holders of both the sample and the reference at the same temperature which is prescribed by the program. Sample and reference are in good thermal contact with their holders. The heat flow differences are recorded as a function of the average holder temperature. As to X-ray analysis, we applied Debye-Scherrer and Bragg-Brentano techniques for structure investigation.

3. RESULTS

The DSC thermogram of red amorphous selenium just prepared is shown in Fig. 1(a). The endothermic peak starting at 30°C is caused by the transition of red to black amorphous selenium. The exothermic process at 80°C represents the transformation into the trigonal modification and at 220°C the crystalline phase melts.

Our experiments showed that the crystallization behaviour changes with time and depends very much on the storage temperature of the samples. A complete change of phenomena occurs at 30°C.

After a storage period of about 30 *d* at

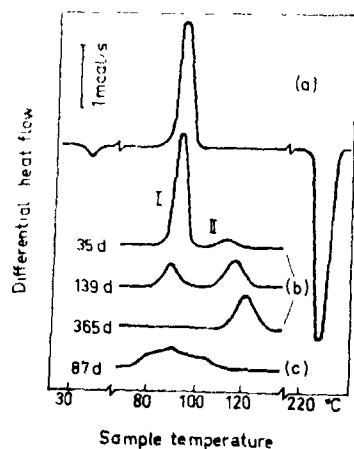


Fig. 1. DSC thermograms of red amorphous selenium, exothermic upward (a) Just prepared; (b) Stored at 25.8°C; (c) Stored at 31.0°C. Sample mass 12.8 mg, scan speed 4°C/min, storage periods indicated

25.8°C, an additional peak (II) with an onset at 106°C could be observed (Fig. 1(b)). The samples kept at 28.4, 23.2, 19.7 and 17.0°C showed this peak II if stored for nearly 5, 60, 80 and 160 *d*, respectively. X-ray analysis revealed that it represents the recrystallization of highly disordered monoclinic selenium into the trigonal modification. The area of peak I decreased in the course of storage time, whereas peak II increased and reached the saturation value after peak I had disappeared (after 200 *d* at 25.8°C) (Fig. 2). Peak II position was found to be independent of storage time and temperature as long as both peaks exist. With the first peak absent,

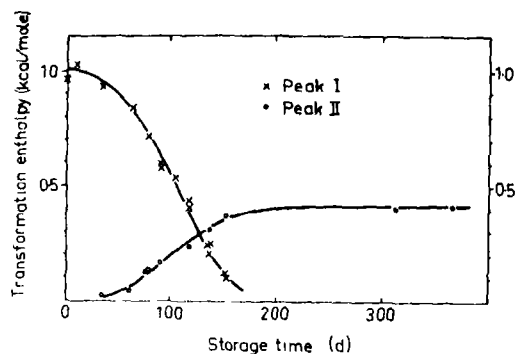


Fig. 2. Enthalpies of the two transformations (I and II, see Fig. 1(b)) vs. storage time. Storage temperature 25.8°C.

however, the second peak is shifted to higher temperatures with increasing storage time indicating the formation of an improved monoclinic crystal structure. X-ray patterns due to the trigonal modification could never be detected on specimens stored below 30°C.

The thermograms of samples stored above 30°C do not show two distinct peaks in the crystallization region (Fig. 1(c)). The single peak which appears is merely broadened. The onset of the crystallization is shifted towards lower temperatures and the total peak area decreases in the course of storage time. X-ray investigations revealed that upon storage above 30°C part of the selenium was converted into the trigonal modification. The fraction

remaining amorphous is a function of the storage time (Fig. 3). The S-shaped curves are similar to those found for high polymers[10]. After 90–100 d the crystal growth becomes very slow. The value then reached is strongly dependent on the crystallization temperature. This behaviour suggests that the polymer consists of chains with high molecular weight[11].

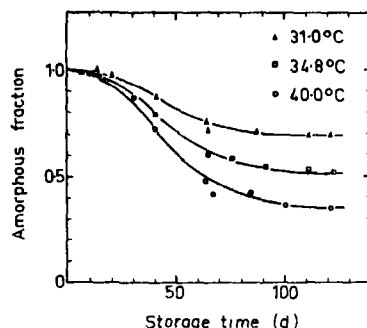


Fig. 3 Amorphous fraction vs. storage time. Storage temperatures indicated.

4. DISCUSSION

Monoclinic selenium is known to be a molecular crystal composed of Se_8 ring molecules. By means of CS_2 extraction measurements Briegleb[12] suggested that red amorphous selenium also consists of Se_8 rings (in his paper Se''). Thus the complete conversion of red amorphous selenium into the metastable monoclinic modification below 30°C appears understandable.

The conversion into the stable trigonal modification above 30°C , however, is more difficult to explain because the latter is known to consist of long helical chains. The crystallization behaviour found in this investigation corresponds to that of high polymers[11]. The Se chains are thus thought to be formed by polymerization of Se_8 rings. On the other hand, Das Gupta *et al.*[13] observed complete conversion of originally vitreous selenium into the monoclinic form at the surface of bulk material which had been stored for seven

years at temperatures not higher than 28°C . This fact involves the formation of rings from chains which exist in the vitreous state[14].

The mutual conversion of rings and chains is the essential feature of the theory of Eisenberg and Tobolsky[15]. They predicted a well-defined transition temperature below which only Se_8 rings are assumed to be present and above which the concentration of these rings decreases due to the formation of polymer chains. In a previous paper[16], they applied their theory to sulfur describing its behaviour over the entire liquid range including the transition temperature of 159°C . They calculated the corresponding temperature of selenium as 83°C , i.e. it lies below the melting point of the trigonal modification (220°C) and might be inobservable as they assume, probably because of crystallization effects. It is known, however, that liquid selenium is easily supercooled so that the transition should be detectable. In spite of this it has not yet been observed.

We assume that the temperature of $30 \pm 1^\circ\text{C}$ above and below which the crystallization behaviour was found to be fundamentally different is the transition temperature discussed. Regarding the uncertainty of the value calculated by Eisenberg and Tobolsky the temperature is not in contradiction to the theory. Red amorphous selenium thus seems to be identical with the supercooled liquid consisting almost exclusively of Se_8 rings.

A relationship to the phenomenon of the glass transformation which is usually found at about $T_g = 30^\circ\text{C}$ does not exist. Dzhililov and Rzaev[17] showed that T_g is lowered to 23.5°C if the selenium is cooled with $0.005^\circ\text{C}/\text{min}$. In contrast to sulfur[18], however, their volume temperature curve which yields $T_g = 23.5^\circ\text{C}$ does not show any characteristic change at 30°C . On cooling, the ring-chain equilibrium (i.e. increasing Se_8 ring concentration with decreasing temperature) is obviously reached more slowly than the metastable configurational arrangement of the

molecules in the supercooled liquid, the freezing of which causes the formation of the glass. Another indication for the slow Se_8 ring formation on cooling and for the existence of chains even at $T_g = 23.5^\circ\text{C}$ is suggested by Eisenberg's estimation of the glass transformation of the pure amorphous Se_8 which yielded -50°C [19].

Acknowledgements – The authors are indebted to P. Franz and K. Hamann for helpful discussions.

*H. Physikalisches Institut,
Technische Universität,
Berlin,
Germany*

H. GOBRECHT
G. WILTERS
D. WOBIG

REFERENCES

1. MONDAIN-MONVAL P., *Annls. Chim.* 3, XI, 5 (1935).
2. RICHTER H., KULICKI W. and SPECHT H., *Z. Naturf.* 7a, 511 (1952).
3. LUCOVSKY G., MOORADIANA, FAYLOR W., WRIGHT G. B. and KEIZER R. C., *Solid State Commun.* 5, 113 (1967).
4. KAPLOW R., ROWE J. A. and AVERBACH B. I., *Phys. Rev.* 168, 1068 (1968).
5. GATTOW G., *Z. anorg. allg. Chem.* 317, 245 (1962).
6. GATTOW G. and HEINRICH G., *Z. anorg. allg. Chem.* 331, 275 (1964).
7. PREUNER G. and BROCKMÜLLER J., *Z. phys. Chem.* 81, 129 (1913).
8. PEIBST H. and AMMON G., *Phys. Status Solidi* 10, 227 (1965).
9. GOBRECHT H., BRATFER P., WILTERS G. and BAUMS., *J. Rad. Chem.* 5, (1970).
10. BANKS W., GORDON M., ROE R.-J. and SHARPLESA, *Polymer* 4, 61 (1963).
11. STUART H. A., *Physik der Hochpolymeren*, Vol. 3, p. 530. Springer, (1955).
12. BRIEGLEB G., *Z. phys. Chem. A* 144, 321 (1929).
13. DAS GUPTA K., DASS R. and RAY B. B., *Indian J. Phys.* 15, 389 (1941).
14. VAN AKEN J. E., PRINS J. A., REINHART R. and TUINSTRA F., *Mater. Res. Bull.* 3, 219 (1968).
15. EISENBERG A. and TOBOLSKY A. V., *J. polymer Sci.* 46, 19 (1960).
16. TOBOLSKY A. V. and EISENBERG A., *J. Am. chem. Soc.* 81, 780 (1959).
17. DZHALILOV S. U. and RZAEV K. I., *Phys. Status Solidi* 20, 261 (1967).
18. FEHR F. and HELLWIG E., *Z. anorg. allg. Chem.* 294, 63 (1958).
19. EISENBERG A., *Polymer Lett.*

J. Phys. Chem. Solids Vol. 31, pp. 2148–2151.

Electrical conductivity of thin single crystals of the IVB–VIB dichalcogenides

(Received 22 September 1969;

in revised form 30 January 1970)

PREVIOUS measurements[1–8] of the conductivity of the transition metal (IVB–VIB) dichalcogenides were limited to thick samples or to compacts. Measurements on thin single crystals ($\leq 10^{-5}$ cm) are presented in this note. The results are consistent with the proposed energy-band model of Connell, Wilson and Yoffe[9] and suggest that the conductivities of synthetic MoS_2 and MoSe_2 are intrinsic at room temperature.

The IVB–VIB dichalcogenides are layer compounds which have trigonal prismatic or octahedral co-ordination[10]. The polytypes of interest are the two-layered hexagonal (2H) and three-layered rhombohedral (3R) ones[11,12]. Synthetic crystals of several compounds (Table 1) were grown by a halogen-vapor transport method and the structures identified by the electron-microscope or X-ray diffraction patterns; MoS_2 (2H) and WS_2 (3R) were available as natural crystals. The purity of the elements was 5N for the chalcogens; 4N for molybdenum, tungsten, and rhenium; 2N5 for niobium; and 3N for hafnium (apart from 3 per cent zirconium). Thin samples were prepared by cleaving the larger crystallites with "Sellotape", freeing the crystals from the tape in a trichloroethylene bath, and mounting them on sapphire substrates.

Evaporated gold contacts were found to be injecting for all the compounds of Table 1 except WSe_2 (2H). The exception is surprising since Fivaz and Mooser[2] apparently had no problems with gold contacts on WSe_2 crystals grown by the same bromine transport

method. Injecting contacts were obtained by doping WSe_2 with the group VII metal rhenium (< 0.3 wt. % by analysis).

Space-charge injection by the contacts was observed at low temperatures in MoS_2 , MoSe_2 and MoTe_2 . The current-voltage relations could be accurately described by the equation

$$I = GV + \beta V^\delta$$

where I is the current, G is the Ohm's-law conductance of the crystal, V is the voltage, and β and δ are empirically determined parameters (δ varied between 2.0 and 3.6 over the range 30–90°K). The values obtained for β and δ did not support the existence of either a single level or an exponential distribution of traps in the forbidden zone[13].

Two experimental difficulties in measuring the conductivity of the layer compounds should be mentioned. Measurements of the conductivity normal to the c -axis are usually made with the contacts attached to the basal plane, as the other surfaces are marred by defects at the edges of the layers. Since the crystals are highly anisotropic, the contact gap must be much larger than the crystal thickness, in order to avoid errors in measurement. In MoS_2 , which is the only crystal whose anisotropy has been measured, $\sigma_\perp/\sigma_\parallel = 10^2$ to 10^3 [7, 14, 15], where $\sigma_\perp$ and $\sigma_\parallel$ are the conductivities normal and parallel to the c -axis. All the thin crystals investigated had inter-contact areas which were about 2×10^{-2} cm wide and 5×10^{-3} cm long; hence the contact gap l was about 10^3 times larger than the crystal thickness d (measured interferometrically to within ± 50 Å). The l/d ratio is usually much smaller for thick crystals. The other experimental difficulty is caused by structural defects within thick samples[4]. However, thin crystals ($\leq 10^{-5}$ cm) are normally free from such defects; this is easily verified by examining the crystals under a microscope.

Table 1 gives the results of the conductivity

measurements. (In parentheses in the Table is given the range of conductivity values for the number of samples measured.) The values for MoS_2 (both 2H and 3R) are an order of magnitude larger than those reported by Fivaz and Mooser[2] and Evans and Young[7], and imply that the carrier concentration at room temperature is about $2 \times 10^{17} \text{ cm}^{-3}$ (the carrier mobility is assumed to be $10^2 \text{ cm}^2/\text{V sec}$ [2, 4]). The $\text{WS}_2(3\text{R})$ and $\text{WSe}_2:\text{Re}(2\text{H})$ values are the first to be reported. It is clear from the Table that the thin-crystal conductivities of the group VIB compounds tend to be larger than those previously reported. These differences can

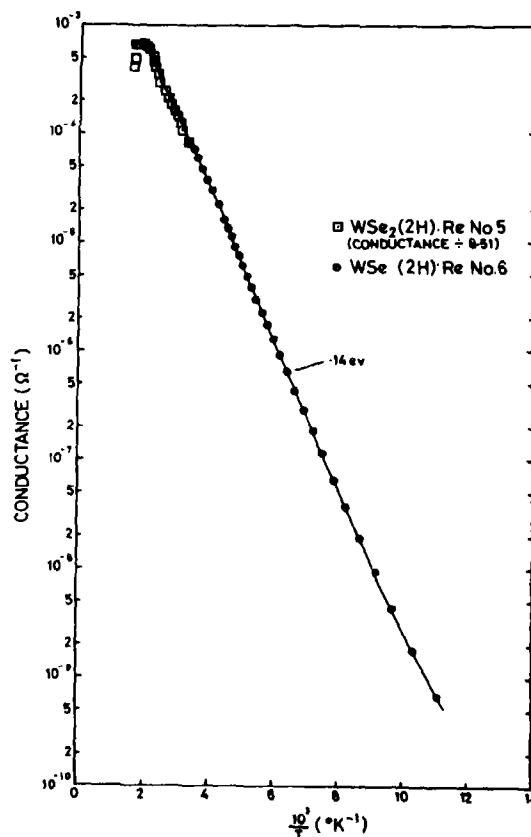


Fig. 1. Variation of conductance with temperature for $\text{WSe}_2:\text{Re}(2\text{H})$. Above 500°K crystal No. 5 began to decompose.

Table 1. Crystal preparation and room-temperature conductivities normal to the c-axis. References are given in brackets. The conductivity value of Ref. [5] is for a sintered compact of NbSe₂

Crystal	Crystal growth	Number of samples	This work: Room temperature conductivity ($\Omega^{-1}\text{cm}^{-1}$)	Other published results on conductivity ($\Omega^{-1}\text{cm}^{-1}$)
MoS ₂ (2H)	Natural (Japanese)	4	3.7 (0.6-7.9)	0.078 [7] 2.2 [4]
MoS ₂ (3R)	Bromine transport	4	3.4 (2.9-3.8)	0.13 [2]
MoSe ₂ (2H)	Bromine transport	4	2.3 (1.3-3.1)	0.65 [2]
α -MoTe ₂ (2H)	Bromine transport	2	1.4 (1.2-1.6)	5 [8]
WS ₂ (3R)	Natural (Italian)	1	10	
	Iodine transport	1	24	
WSe ₂ (2H)	Iodine transport	6	-	0.78 [2]
WSe ₂ -Re(2H)	Iodine transport	2	24 (12-36)	
NbSe ₂ (2H)	Iodine transport	1	850	2900 [5]
HfS ₂	Iodine transport	1	6×10^{-9}	3×10^{-8} [6]

probably be traced to the structural defects of thick crystals and the large electrical anisotropy.

The molybdenum dichalcogenides showed typical semiconductor behavior below room temperature; the results were similar to those obtained by others [2, 4, 7, 8]. The conductance of WSe₂-Re(2H) varied much more strongly over the temperature range 90-500°K (Fig. 1); the 0.14 eV activation energy probably identifies the rhenium donor level. By contrast NbSe₂(2H) showed metallic behavior between room and liquid-nitrogen temperatures (Fig. 2).

The conductivities of Table 1 (both thin- and thick-crystal) are consistent with the optical energy-band model proposed by Connell, Wilson, and Yoffe [9]. In this model the interaction between neighboring transition-

metal atoms is strong enough to form narrow *d*-like non-bonding bands which lie within the basic bonding gap. The extent to which these bands are occupied determines the electrical properties of the compounds. Transport measurements on synthetic MoS₂ [2] have shown that the Hall activation energy and carrier mobility above 200°K do not vary greatly from sample to sample; thus the narrow thermal gap (≈ 0.3 eV) between the non-bonding bands, which the optical model proposes, suggests that the conductivity of MoS₂ at room temperature is intrinsic, rather than extrinsic [2]. The basic equation for intrinsic conductivity can be satisfied by using a thermal gap of 0.32 eV [2], effective masses equal to the free electron mass (the *d*-bands are narrow), mobilities $\approx 10^2$ cm/V sec [2], and the MoS₂(3R) conductivity

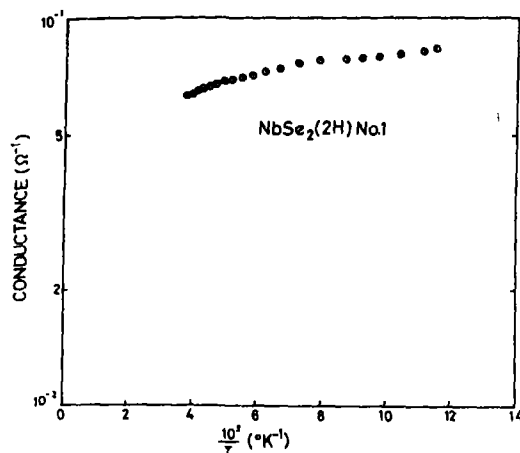


Fig. 2. Variation of conductance with temperature for NbSe₂(2H).

value of Table 1. It is important to note that this (intrinsic) interpretation is valid only if the high-conductivity value obtained on thin single crystals is used. The transport data on MoSe₂ can be similarly interpreted.

Lepetit's work [8] on MoTe₂ appears to be inconsistent with the optical model. His Hall and Seebeck data represent an impurity-controlled semiconductor that has an intrinsic gap of 1.0 eV (the optical gap is also 1 eV [16]). However, Revolinsky and Beerntsen [17] have observed that MoTe₂ loses tellurium above 600°K. Since Lepetit's conductivity activation energy of 1.0 eV occurs above 750°K, his results may have been affected by this loss. If the data are correct, however, the *d*-bands in MoTe₂ may lie outside the bonding gap or be too narrow to support band conductivity.

Acknowledgement—The author is grateful to Dr. A. D. Yoffe for many useful discussions.

Cavendish Laboratory,
University of Cambridge,
England

T. J. WIETING*

*Present address: Code 6477A, Naval Research Laboratory, Wash. D. C. 20390, U.S.A.

REFERENCES

1. KERSHAW R., VLASSE M. and WOLD A. J., *Inorg. chem.* **6**, 1599 (1967).
2. FIVAZ R. and MOOSER E., *Phys. Rev.* **163**, 743 (1967).
3. FRINDT R. F. and YOFFE A. D., *Proc. R. Soc. A* **273**, 69 (1963).
4. MANSFIELD R. and SALAM S. A., *Proc. phys. Soc. B* **66**, 377 (1952).
5. BRIXNER L. H. J., *inorg. nucl. Chem.* **24**, 257 (1962).
6. CONROY L. E. and PARK K. C., *J. inorg. Chem.* **7**, 450 (1968).
7. EVANS B. L. and YOUNG P. A., *Proc. R. Soc. A* **284**, 402 (1965).
8. LEPETIT, A. J., *Phys. Radium*, **26**, 175 (1965).
9. CONNELL G. A. N., WILSON J. A. and YOFFE A. D., *J. Phys. Chem. Solids* **30**, 287 (1969); CONNELL G. A. N., WIETING T. J., WILSON J. A. and YOFFE A. D., *Proc. Int. Conf. Phys. Semiconduct., Moscow*, p. 414 (1968).
10. JEI LINEK F., *Ark. Kemi* **20**, 477 (1963).
11. ZVYAGIN B. B. and SOBOLEVA S. V., *Soviet Phys. Cryst.* **12**, 46 (1947).
12. JEI LINEK F., BRAUER G. and MÜLLER H., *Nature, Lond.* **185**, 376 (1960).
13. ROSE A., *Phys. Rev.* **97**, 1538 (1955).
14. DUTTA A. K., *Nature, Lond.* **159**, 477 (1947).
15. DEY A. P., *Proc. natn. Acad. Sci. India* **14**, 47 (1944).
16. WIETING T. J. and YOFFE A. D., *Phys. Status Solidi* **37**, 353 (1970).
17. REVOLINSKY E. and BEERNTSEN D. J., *J. Phys. Chem. Solids* **27**, 523 (1966).

J. Phys. Chem. Solids Vol. 31, pp. 2151–2154.

Conduction electron hyperfine interaction in semiconducting CdS*

(Received 1 December 1969;

in revised form 13 January 1970)

BLOEMBERGEN [1] has calculated the nuclear spin-lattice relaxation time, T_1 , due to the contact hyperfine interaction with nondegenerate conduction electrons:

*Sponsored by the Aerospace Research Laboratories, Office of Aerospace Research, United States Air Force, Contract No. F33615-67-C-1027.

$$(T_1)^{-1} = 2(2\pi)^{-3/2} \hbar^{-4} N l (m_1 m_2 m_3)^{1/2} (kT)^{1/2} \times V_{at}^2 a^2 \quad (1)$$

where $\hbar$ is Planck's constant divided by 2π ; N is the conduction electron density; l is the number of equivalent minima in the conduction band; m_1 , m_2 , m_3 are the anisotropic effective masses; k is Boltzmann's constant; T is the absolute temperature; V_{at} is the atomic volume (molecular weight/density $\times$ Avogadro's number); and a is the hyperfine constant given by (in ergs),

$$a = (8\pi/3) \gamma_e \gamma_n \hbar^2 \langle |\phi_f(0)|^2 \rangle. \quad (2)$$

Here γ_e and γ_n are, respectively, the electronic and nuclear gyromagnetic ratios, and $\langle |\phi_f(0)|^2 \rangle$ is the averaged electronic probability density at the nucleus, with normalization to unity in V_{at} . Equation (1) contains a factor four correction given by Abragam [2]. The purpose of this paper is to report, for the first time, the value of $\langle |\phi_f(0)|^2 \rangle$ in *n*-type wurtzite CdS; this can be compared with band-theory calculations of this quantity, when available.

The CdS sample was a cylindrical crystal, 9 mm in dia. and 18 mm in length, grown from the melt. Both electrical and NMR measurements were carried out on the same sample. For the electrical measurements five indium leads were soldered on and the crystal current, crystal voltage (parallel to current), and Hall voltage (perpendicular to current and magnetic field) were measured as a function of temperature. From these quantities were calculated [3] the resistivity (ρ) and Hall mobility (μ_H). The carrier concentration (N), in cm^{-3} , was then found from the relationship $N = K (6.25 \times 10^{16}) / (\rho \mu_H)$, where ρ is expressed in ohm-cm, μ_H in $\text{cm}^2/(\text{v})\text{sec}$ and K is a factor between 1–2 which depends upon the degree of degeneracy of the electrons and also upon the relative amounts of lattice-vibration scattering and ionized-impurity scattering [4]. The μ_H vs. T plot shows no significant impurity scattering and can be fitted quite well, as shown in Fig. 1, by assuming a combination of

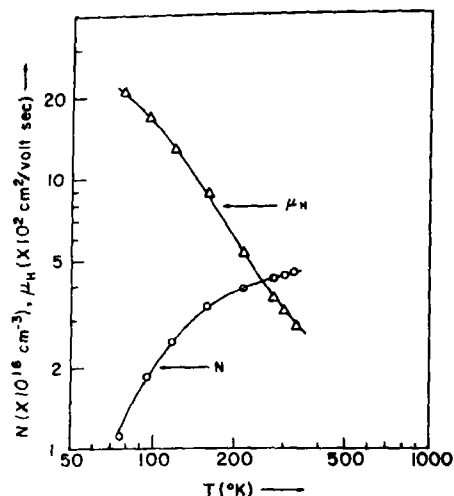


Fig. 1 The Hall mobility, μ_H and the carrier concentration, N , as functions of temperature in single-crystal CdS. The solid lines are theoretical fits: N is fitted according to equation (4.45) of Ref. [3], μ is fitted according to $\mu^{-1} = \mu_{opt}^{-1} + \mu_{piez}^{-1}$, where the polar optical-mode contribution, $\mu_{opt} = 175 (e^{-3850/T} - 1)$, and the piezoelectric-potential contribution, $\mu_{piez} = 2.0 \times 10^4 T^{-1/2}$.

polar optical-mode scattering and acoustical-mode piezoelectric scattering. Furthermore the temperature dependence of the product $\rho \mu_H$ clearly indicates nondegeneracy and thus we used $K = 3\pi/8$. The N vs. T curve was fitted with a formula [5] derived from a model in which the electrons are thermally excited from a shallow donor level. The best fit, shown in Fig. 1, gave parameters $N_D = 7.8 \times 10^{16} \text{ cm}^{-3}$, $N_A = 3.0 \times 10^{16} \text{ cm}^{-3}$, and $E_D = 0.016 \text{ eV}$, where N_D is the number of donors, N_A is the number of acceptors, and E_D is the energy difference between the donor level and conduction band.

The T_1 's were measured by a direct method using a Varian V-4200B wideline NMR spectrometer. First the spin system was saturated at resonance, then the magnetic field was moved off resonance for a time t , and finally the field was swept back through the resonance to measure the magnetization recovered in time t . This sequence of operations was accomplished manually although it could be done electronically also. The dispersion mode

was used with high r.f. field strengths since it was difficult to even observe the absorption mode. The amplitude of the signal as a function of t obeyed $M(t) = M(\infty)[1 - e^{-t/T_1}]$, and the calculated T_1 was independent of r.f. field strength, modulation field strength, or sweep time, as long as the following conditions were observed: (1) the static field was held at resonance long enough to completely saturate the spin system (the time required was less than 1 sec); (2) the off-resonance field, at which the magnetization recovered, was chosen far enough from the resonance field to avoid saturation; (3) the sweep time, for observation of the resonance, was much less than T_1 . This method of measurement compared favorably when checked against the pulsed r.f. method on H^1 in H_2O and other samples. Similar techniques, using fast passage, dispersion mode, and high r.f. and modulation field strengths, have been employed[6] before.

Temperature regulation for both the NMR and electrical measurements was accomplished with a Varian V-4257 variable-temperature accessory.

The data for T_1 and the product T_1N are plotted as a function of temperature in Fig. 2. It is seen that $T_1N \propto T^{-1/2}$ in the region $T = 175\text{--}350^\circ\text{K}$. Also T_1 is independent of frequency, ν , in this region so that both the temperature and frequency dependence of T_1 satisfy equation (1). At 300°K T_1 vs. ν was investigated from 2 to 15 MHz and less than 10 per cent variation was found, random and within the experimental precision. The fall-off of T_1N vs. T below 175°K is most likely due to another relaxation mechanism, paramagnetic impurities, becoming effective. Supporting this is the fact that T_1 shows a slight frequency dependence at 77°K .

At 300°K the measured values of T_1 and N are $T_1 = (46 \pm 2)$ sec, $N = (4.4 \pm 0.2) \times 10^{16}$ cm^{-3} . Using known values for the other parameters, $l = 1$, and [7] $(m_1, m_2, m_3) = (0.18 \pm 0.02)m_p$, we calculate from equations (1) and (2), $a = (0.34 \pm 0.03) \text{ cm}^{-1}$. Also, $\gamma_n = 5.93 \times$

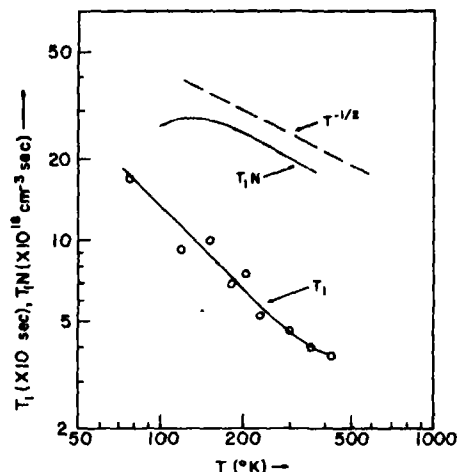


Fig. 2. The nuclear spin-lattice relaxation time T_1 , at 8 MHz, and the product T_1N as functions of temperature in single-crystal CdS

10^3 and, using the measured[8] g -value of 1.78, $\gamma_e = 1.57 \times 10^7$, giving $\langle |\phi_F(0)|^2 \rangle = (7.7 \pm 0.6) \times 10^{25} \text{ cm}^{-3}$.

These values can be compared with those for the atomic case. Considering the ionic-solid approximation the appropriate atomic configuration resembling a conduction electron on a Cd^{2+} ion is $4d^{10}5s^2S_{1/2}$. The proper term parameters, including relativistic corrections, yield, using the Goudsmit formula[9], $\langle |\phi_A(0)|^2 \rangle = 9.2 \times 10^{25} \text{ cm}^{-3}$. The ratio $\xi \equiv \langle |\phi_F(0)|^2 \rangle / \langle |\phi_A(0)|^2 \rangle \approx 0.84$ is not untypical of metals and semiconductors. Non-contact interactions have been neglected in this approximation due to the fact that they are expected to be small compared to the contact term; in fact, band calculations[10] indicate that the conduction electrons in CdS are quite like the atomic $5s$ electrons in Cd with less than 10 per cent p character. It remains for theorists to explicitly calculate $\langle |\phi_F(0)|^2 \rangle$ in order to compare with the experimental value given in this paper.

Research Institute,
University of Dayton,
Dayton,
Ohio 45409, U.S.A.

D. C. LOOK

REFERENCES

1. BI OMBERGEN N., *Physica* **20**, 1130 (1954).
2. ABRAGAM A., *The Principles of Nuclear Magnetism*, p. 390. Oxford University Press, London (1961).
3. See, for example, PUTLEY F. H., *The Hall Effect and Related Phenomena*, pp. 23, 24. Butterworth, London (1960).
4. See, for example, BUBL R. H., *Photoconductivity of Solids*, pp. 261, 262. Wiley, New York (1960).
5. Ref. [3], p. 124.
6. SHUIMAN R. G. and WYLU DAB J., *Phys. Rev.* **103**, 1127 (1956).
7. This range of effective masses includes almost all the measured values. See, for example, ZOOK J. D. and DEXTER R. N., *Phys. Rev.* **129**, 1980 (1963); BAER W. S. and DEXTER R. N., *Phys. Rev.* **135**, A1388 (1964); KOBAYASHI K., in *International Conference on III-V Semiconducting Compounds* (Edited by D. G. Thomas), p. 755. Benjamin, New York (1967).
8. LAMBE F. and KIKUCHI C., *J. Phys. Chem. Solids* **9**, 492 (1958).
9. GOLDSMITH S., *Phys. Rev.* **43**, 636 (1933).
10. COLLINS T. C. (private communication).

J. Phys. Chem. Solids, Vol. 31, pp. 2154-2157

The effect of rigidity and density on the temperature variation of Mössbauer effect

(Received 22 August 1969)

in revised form 8 December 1969)

THE MODULUS of rigidity and the density of solids are two strongly temperature dependent parameters. These two parameters have been shown to be involved in the recoilless resonance emission of γ -rays. Through these parameters, the influence of temperature on f has been calculated for the 14.4 keV. transition of ^{57}Fe in some host lattices in the region of low ($T \ll \theta_D$) and high ($T \gg \frac{1}{2}\theta_D$) temperatures. It has been assumed that the forces between impurity and host atoms are the same as those between host atoms. The temperature variation so obtained is in general agreement with the variation obtained by Mahesh[1]. Our calculated results for ^{57}Fe in Cu and Au

hosts are in good agreement with the experimental values of Steyert and Taylor[2] and Housley *et al.*[3] (for Cu) except in the high temperature range. It is noticed that the decrease in f for the same temperature change is greater for lattices having large values of the temperature coefficient of modulus of rigidity. Although no definite relationship may be ascertained, there is a strong correlation between the temperature variation of f and the rigidity.

The recoilless fraction f is expressed as [4],

$$f = \exp [-K^2 \langle x^2 \rangle] \quad (1)$$

where $K = E/\hbar c$, E being the γ -ray energy and $\langle x^2 \rangle$ is the component of the mean square vibrational amplitude of the emitting nucleus in the direction of the γ -rays.

In our case, the ^{57}Fe source is embedded as an impurity in different host lattices, so that $\langle x^2 \rangle$ is the mean square vibrational amplitude of impurity. Assuming the same binding forces as between host atoms, $\langle x^2 \rangle$ is given by [3],

$$\langle x^2 \rangle = \langle x^2 \rangle_{\text{host}} \quad \text{for } T \gg \theta_D \quad (2)$$

$$\langle x^2 \rangle = (M/M')^{1/2} \langle x^2 \rangle_{\text{host}} \quad \text{for } T \rightarrow 0 \quad (3)$$

where M and M' are the masses of host and impurity atoms respectively.

With the help of equations (2) and (3), equation (1) can be written for low ($T \ll \theta_D$) and high ($T \gg \frac{1}{2}\theta_D$) temperature ranges respectively as,

$$f = \exp [-K^2 \langle x^2 \rangle_{\text{host}} (M/M')^{1/2}] \quad (4)$$

$$f = \exp [-K^2 \langle x^2 \rangle_{\text{host}}]. \quad (5)$$

Assuming the Debye model of the phonon spectrum, $\langle x^2 \rangle_{\text{host}}$ can be written as a function of temperature T as [4],

$$\langle x^2 \rangle_{\text{host}} = \{3\hbar^2/4M k\theta_D\} \left\{ 1 + 4T^2/\theta_D^2 \int_0^{\theta_D/T} u du/e^u - 1 \right\}. \quad (6)$$

The integral in equation (6) can be exactly solved near absolute zero giving the value of $\langle x^2 \rangle_{\text{host}}$ as [4],

$$\langle x^2 \rangle_{\text{host}} = \{3\hbar^2/4Mk\theta_D\} \{1 + 2\pi^2 T^2/3\theta_D^2\}. \quad (7)$$

With the help of equation (7), equation (4) in the limit $T \rightarrow 0$ can be transformed as,

$$f = \exp [-3E^2/4\sqrt{MM'} c^2 k\theta_D]. \quad (8)$$

Using the infinite series expansion of the integral [5] in equation (6) we obtain,

$$\langle x^2 \rangle_{\text{host}} = \{3\hbar^2/4Mk\theta_D\} \{ (4T/\theta_D) + \frac{1}{9}(\theta_D/T) + \dots \}. \quad (9)$$

In the range of high temperature ($T \gg \frac{1}{2}\theta_D$) equations (9) and (5) would yield an expression for the value of f as,

$$f = \exp [-3E^2 T/Mc^2 k\theta_D^2]. \quad (10)$$

In the above cases θ_D is the Debye temperature of the host (near 0°K) defined by [6],

$$\theta_D = (h/k) \cdot M_z \cdot S \quad (11)$$

where,

$$M_z = (3\rho N_p/4\pi m)^{1/3}$$

here ρ , m , p , N and S are respectively, density (near 0°K), molecular wt., atomicity, Avogadro's number and mean value of sound velocity (near 0°K). Combining equations (11) and (8), we get a relation for f near 0°K

$$\log f = -3E^2/4\sqrt{MM'} \cdot c^2 \cdot h \cdot M_z \cdot S. \quad (12)$$

Similarly combining equations (11) and (10), an expression for f at high temperatures ($T \gg \frac{1}{2}\theta_D$) can be obtained

$$\log f = -3E^2 \cdot k \cdot T/M \cdot c^2 \cdot h^2 \cdot M_z^2 \cdot S^2. \quad (13)$$

From equations (12) and (13), it is evident that the variation of f with T depends upon the change of S and ρ with temperature T . As the sound velocity is the square root of the elastic modulus and density, the mean sound velocity S can be expressed as,

$$S = \sqrt{G_0/\rho}$$

where G_0 is the mean value of the elastic modulus near 0°K. If we assume that the variation of G_0 with temperature is similar to that of the modulus of rigidity [7], then

$$S_t = \sqrt{G_0(1-A \cdot T)/\rho(1-\beta \cdot T)}. \quad (14)$$

Here β is the coefficient of volume expansion and A is the temperature coefficient in the expression $G_t = G_0(1-A \cdot T)$, where G_t and G_0 are the moduli of rigidity at temperature T and absolute zero respectively.

Substitution of equation (14) in equation (12) therefore yields an expression for the variation of f with T at very low temperatures ($T \ll \theta_D$) as,

$$\log f_{t \ll \theta_D} \approx -3E^2 \{1 + T/2(A - \beta/3)\} / 4\sqrt{MM'} \cdot c^2 \cdot h \cdot M_z \cdot S \quad (15)$$

where higher order terms in T have been ignored.

A similar relation at high temperatures ($T \gg \frac{1}{2}\theta_D$) can be derived by the combination of equations (14) and (13), which would then give the f - T variation as,

$$\log f_{t \gg \theta_D} \approx -3E^2 \cdot k \cdot T \{1 + T(A - \beta/3)\} / M \cdot c^2 \cdot h^2 \cdot M_z^2 \cdot S^2. \quad (16)$$

Here we have neglected terms involving the product of $A \cdot \beta$, since A and β are very small.

Equations (15) and (16) give the f - T variation close to absolute zero ($T \ll \theta_D$) and at high temperatures ($T \gg \frac{1}{2}\theta_D$) respectively. These variations have been

calculated for the 14.4 keV gamma transition of ^{57}Fe in Cu, Au, Al and Ag at temperatures 4, 293, and 773°K (Fig. 1) using the values of S , β , A and ρ (Refs. [6, 8, 9]) for these host lattices. The calculated results for Cu and Au up to 300°K are in agreement with the experimental values of Steyert and Taylor[2] and Housley *et al.* [3] (for Cu). Our results are about 10 per cent lower than those of experiments[2, 3] at high temperatures. The reason for this is not quite clear, but it may be due to the deviation from a linear variation of the rigidity at high temperature. Experimental data for Al and Ag have not been reported as far as known to us.

rigidity of the lattice with temperature plays a prominent part in $f-T$ variation and that the density plays a secondary role.

In Fig. 2, an overall decrease in $\Delta \equiv [f(t)_{t=4^\circ\text{K}} - f(t)_{t=293^\circ\text{K}}]$ in f of Pt, Pd, Au, Cu (from experimental data[2]), Ag, Al (from theoretical calculations) and Sn (for 23.9 kev. transition in ^{119}Sn [10]) is plotted against the corresponding values of A . In general the decrease is greater for the same temperature change as A increases, but there is no definite relationship. This indicates that the temperature coefficient of the modulus of rigidity plays an effective role in the temperature variation of f , such that the decrease in

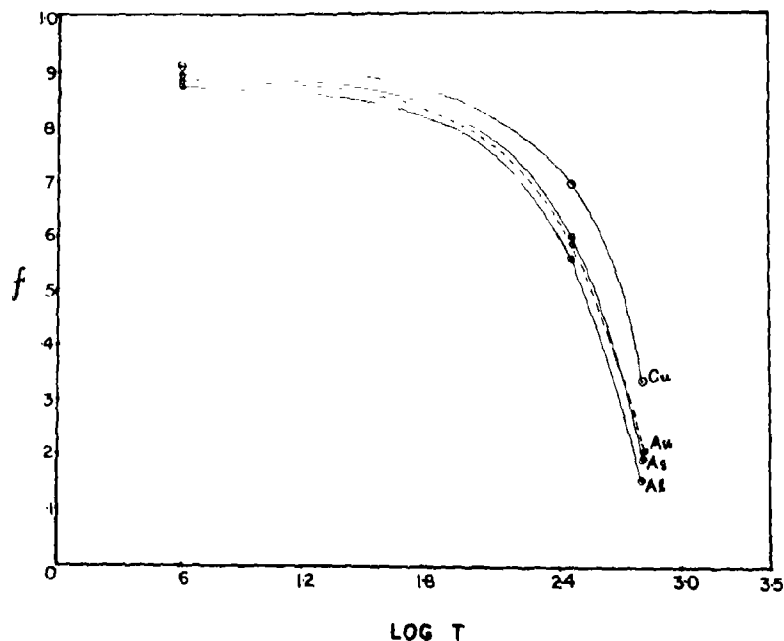
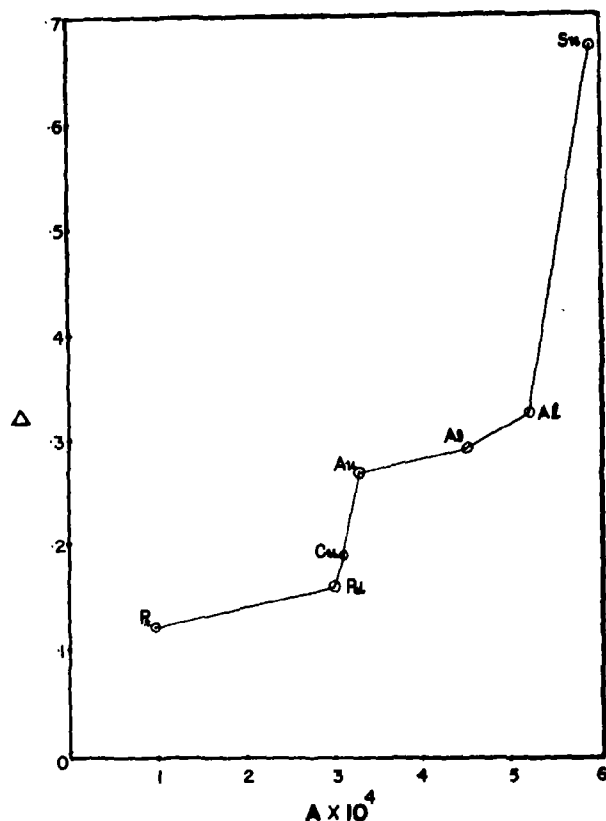


Fig. 1 Variation of f as a function of $\log T$ for ^{57}Fe (14.4 keV transition) in Au, Cu, Al and Ag hosts

The magnitude of A is of the order of 10^{-4} and that of β is of the order of 10^{-6} , which is much smaller than A used in equations (15) and (16). It shows that the variation of

rigidity is responsible for $f-T$ variation. A similar argument can be given for the increase in f with pressure on the basis of the increase in the lattice rigidity[11].

Fig. 2 Variation of Δ as a function of A .

Acknowledgements—Our grateful thanks are due to Dr. K. Mahesh for helpful discussion and to Dr. D. D. Pant and Dr. V. Puri for their interest in the progress of this work. We are also thankful to Dr. S. D. Sinhwai for providing the facilities of the State Observatory Library. We wish to acknowledge referee for making some useful suggestions.

Department of Physics, B. N. SRIVASTAVA
D S.B. Government College, R. N. TYAGI
Naini Tal.
India

REFERENCES

1. MAHESH K., *Nucl. Instrum. Meth.* **65**, 349 (1968).
2. STEYERT W. A. and TAYLOR R. D., *Phys. Rev.* **134**, A716 (1964).
3. HOUSLEY R. M., DASH J. G. and NUSSBAUM R. H., *Phys. Rev.* **136**, A464 (1964).
4. WERTHEIM G. K., *Mössbauer Effect: Principles and Applications*, p. 10, 42. Academic Press, New York (1968).
5. MAHESH K., *Nucl. Instrum. Meth.* **54**, 212 (1967).
6. ANDERSON O. L., *Physical Acoustics, Principles and Methods*. (Edited by W. P. Mason), Vol. 3, Part-B, p. 45, 85. Academic Press, New York (1968).
7. Since mean sound velocity S is very close to shear velocity (Ref. [6]), therefore it seems more appropriate to assume the variation of mean elastic modulus with temperature similar to that of the modulus of rigidity.
8. *International Critical Tables*, Vol. 2. McGraw-Hill, New York (1927).
9. KAYE G. W. C. and LABY T. H., *Tables of Physical and Chemical Constants*, p. 33. Longmans Green, London (1959).
10. HOHENEMSER C., *Phys. Rev.*, **139**, A185 (1965).
11. MEHESH K., *Ind. J. pure. appl. Phys.* **4**, 480 (1966).

On the magnetic structure of U_3P_4 and U_3As_4

(Received 21 November 1969)

IN RECENT years several studies of magnetic properties of U_3P_4 and U_3As_4 powders, including preliminary neutron diffraction investigations[1], have been undertaken by Trzebiatowski and Troc and their collaborators[2, 3]. It has been found that these compounds become ferromagnetic below T_c , and their paramagnetic and ferromagnetic moments per U ion were established.

Recently Bührer[4] published the results of magnetic measurements made on monocrystalline samples of U_3P_4 and U_3As_4 . It is evident from his data that these crystals exhibit high anisotropy and that the magnetization direction is along the [111] axis. Bührer made also a suggestion, that in this case we are dealing with a rather uncommon type of ferromagnetism, namely that there are three ferromagnetic sublattices with mutually perpendicular directions.

Because we have not, at the moment, any definitive determination of the magnetic structure of these compounds, it may be worthwhile to say a few words about symmetry applied to this problem.

From X-ray analysis (and also from [1]) it is known that U_3P_4 and U_3As_4 crystallize in the Th_3P_4 chemical structure with U ions located at the six symmetry equivalent positions:

$$\begin{aligned} p_1 &= \left(\frac{2}{3} 0 \frac{1}{3}\right), & p_2 &= \left(\frac{1}{3} 0 \frac{2}{3}\right), & p_3 &= \left(\frac{1}{3} \frac{1}{3} 0\right) \\ p_4 &= \left(\frac{2}{3} \frac{1}{3} 0\right), & p_5 &= \left(0 \frac{1}{3} \frac{2}{3}\right), & p_6 &= \left(0 \frac{2}{3} \frac{1}{3}\right). \end{aligned}$$

The origin of the coordinate system is taken on the threefold axis, at the center of the twofold axes.

The symmetry of the paramagnetic state

is described by the grey Shubnikov group— $I43d1'$.

Assuming that the transition to the ferromagnetic state is of the second order in the Landau sense, we have applied the criteria of the Landau theory to predict the magnetic symmetry below T_c . With the help of the table elaborated by Sirotin[5] we arrive at the conclusion that there are two possible ferromagnetic groups:

$$\begin{aligned} \text{case I: } I42'd' - I42d/I4 & \text{ or } Sh_{122}^{337} - D_{2d}^{12}/S_4^2 \\ \text{case II: } R3c' - R3c/R3 & \text{ or } Sh_{161}^{161} - C_{3v}^6/C_3^4 \end{aligned}$$

The Koptsik symbols are given[6] on the right. Using the standard procedure of Opechowski and Guccione[7] we are able to determine the magnetic structures invariant under the symmetry operations of these groups:

Case I. It may be demonstrated[8] that the ferromagnetic structure invariant with respect to this group should be one with the magnetization directed along one of the four-fold axis. But, in view of Bührer's results[4], the magnetization is directed along [111]. Thus the group $I42'd'$ must be ruled out.

Case II. The positions $p_1, \dots, p_6$, which are special ones in the Th_3P_4 structure, become general positions if the symmetry is changed to $R3c'$. The most general invariant structure may be described by the following assignment of the magnetic moment vectors to the lattice sites:

$$p_1 = \begin{pmatrix} u \\ v \\ w \end{pmatrix}, \quad p_2 = \begin{pmatrix} u \\ w \\ v \end{pmatrix}, \quad p_3 = \begin{pmatrix} w \\ u \\ v \end{pmatrix},$$

$$p_4 = \begin{pmatrix} v \\ u \\ w \end{pmatrix}, \quad p_5 = \begin{pmatrix} v \\ w \\ u \end{pmatrix}, \quad p_6 = \begin{pmatrix} w \\ v \\ u \end{pmatrix}.$$

We see that in this way the resulting magnetic moment is directed along [111].

As special cases of this generalized struc-

ture we would like to single out the two following:

$$(a) \quad u = v = w \quad \text{then} \quad p_1 = \dots p_6 = \begin{pmatrix} u \\ u \end{pmatrix}$$

$$(b) \quad v = w = 0, u \neq 0 \quad \text{then}$$

$$p_1 = p_2 = \begin{pmatrix} u \\ 0 \end{pmatrix}, \quad p_3 = p_4 = \begin{pmatrix} 0 \\ u \end{pmatrix},$$

$$p_5 = p_6 = \begin{pmatrix} 0 \\ u \end{pmatrix}.$$

The last is the structure suggested by Buhrer.

It is seen from the high anisotropy [4], from recent dilatometric and resistivity measurements made at Wrocław [9], and also from the above considerations that a distinct change of crystal structure should be expected at T_c . Of course, to establish the exact nature of the magnetic ordering a more definitive neutron diffraction study is necessary. Such investigations are now under way at the Institute of Nuclear Research at Swierk.

Acknowledgements—I am grateful to Dr. R. Troc, Dr. Z. Henkie and Dr. W. Suski for illuminating discussions.

*Institute of Theoretical Physics, J. PRZYSTAWA**
University of Wrocław,
Wrocław,
Cybulskiego 36,
Poland

REFERENCES

1. CISZEWSKI R., MURASIK A. and TROC R., *Phys. Status Solidi* **10**, K85 (1965).
2. TRZEBIATOWSKI W. and TROC R., *Bull. Acad. pol. Sci. Ser. Sci. chim.* **11**, 661 (1963).
3. TRZEBIATOWSKI W., SEPICHOWSKA A. and ZYGMUNT A., *Bull. Acad. pol. Sci. Ser. Sci. chim.* **12**, 687 (1964).
4. BUHRER C. F., *J. Phys. Chem. Solids* **30**, 1273 (1969).
5. SIROTIN YU. I., *Kristallografiya*, **8**, 259 (1963).

*Present address: Laboratory for Theoretical Physics, Joint Institute for Nuclear Research; Head Post Office P.O. Box 79, Moscow, U.S.S.R.

6. KOPTSIK V. A., *Shubnikov Groups*, Moscow University Press. (in Russian) (1966).
7. OPECHOWSKI W. and GUCCIONE R., *Magnetism* (Edited by G. T. Rado and H. Suhl), Vol. 2A, Academic Press, New York (1965).
8. PRZYSTAWA J. and STESLICKI J., *Lectures of the 6th A. Winter School of Theoretical Physics, Karpacz* (1969).
9. HENKIE Z., private communication.

J. Phys. Chem. Solids Vol. 31, pp. 2159-2161.

Linear spin wave theory with single ion anisotropy*

(Received 24 September 1969)

IN A RECENT letter, the authors [1] proposed an explanation for the observed magnetization of a thin iron film in terms of a Heisenberg model with a single ion anisotropy term. The purpose of the present note is to explain the method used to find the spin wave modes of that model and, more generally, to extend the usual prescription for determining spin wave energies to the case of a spin system with single ion anisotropy. The most careful discussion [2] known to us of linear spin wave theory in the presence of single ion anisotropy is incorrect; its inadequacy is glaringly obvious when applied to our model, where it leads to unphysical results.

The Hamiltonian in which we are interested is:

$$\mathcal{H} = -g\mu_B H \sum_i S_i^z - \frac{1}{2} \sum_{ij} J_{ij} S_i \cdot S_j + A \sum_i (S_i^x)^2. \quad (1)$$

The coefficient A is assumed to be positive, but small compared to the J_{ij} , so that the x axis is a 'hard' axis, i.e. the magnetization will lie in the y, z plane. The first term describes a

*Supported in part by the U.S. Air Force Office of Scientific Research, U.S. Air Force, Grant # AF-AFOSR-610-67, and the National Science Foundation.

small magnetic field that stabilizes the spins along the $+z$ direction. The question now arises: For $H \rightarrow 0$, does the anisotropy term produce a gap in the spin wave spectrum? On quite general grounds the answer must be that a gap cannot exist; i.e. the magnetization is free to rotate in the y,z plane, so that any restoring torque must go to zero as the wave vector goes to zero. We have found that the ordinary techniques of linear spin wave theory [2-4] are easily capable of avoiding this necessary result, giving spurious gaps or other incorrect behavior.

The point is to write the equation of motion for a spin deviation operator in the correct form:

$$i \frac{d}{dt} S_i^+ = [S_i^+, \mathcal{H}] = g\mu_B H S_i^+ - \sum_{\delta} J_{\delta} (S_i^z S_{i+\delta}^z + S_{i+\delta}^z S_i^z) + \frac{A}{2} [(2S_i^z - 1) S_i^+ + S_i^+ (2S_i^z + 1)]. \quad (2)$$

In writing equation (2), we have used the spin commutation relations as many times as necessary to bring the raising operators S_i^+ all the way to the right and the lowering operators S_i^- all the way to the left. If we now linearize equation (2) by setting the S_i^z operators equal to the spin S , all matrix elements between states $|S_i^z = S\rangle$ and $|S_i^z = S-1\rangle$ are still given correctly. The spurious results mentioned earlier can be traced to incorrect ordering of products such as $S_i^z S_i^+$ before linearizing. If we wish to go beyond a linear low temperature theory, questions of matrix elements to states with two or more spin deviations arise, and the above remarks must be expanded [5].

From here everything is fairly standard. The linearized, fourier transformed, equations of motion are:

$$i\dot{S}_q^+ = \epsilon_q S_q^+ + \frac{A'}{2} (S_q^+ + S_{-q}^-) \\ -i\dot{S}_{-q}^- = \epsilon_q S_{-q}^- + \frac{A'}{2} (S_q^+ + S_{-q}^-) \quad (3)$$

where $\epsilon_q = S \sum_{\delta} J_{\delta} (1 - e^{i\mathbf{q} \cdot \boldsymbol{\delta}}) + g\mu_B H$; $A' = (2S-1)A$; $S_q^+ = 1/\sqrt{N} \sum_i S_i^+ e^{-i\mathbf{q} \cdot \mathbf{r}_i}$. Note that $A' = 0$ for $S = \frac{1}{2}$, as required by the fact that $(S_i^z)^2$ is then a constant. The solution of equations (3) with time dependence $e^{-i\omega_q t}$ will then be a linear combination of S_q^+ and S_{-q}^- with frequency:

$$\omega_q = \sqrt{\epsilon_q(\epsilon_q + A')}. \quad (4)$$

This is the major result; it satisfies the requirement that $\lim_{\mathbf{q} \rightarrow 0} \omega_q = 0$.

To determine the low temperature thermodynamic properties of this model we can proceed in the usual way, defining the operator $a_q = 1/\sqrt{2S} S_q^+$ and treating a_q as a boson operator; i.e. $[a_q, a_q^\dagger] = 1$. The operators which satisfy the linearized equations of motion (3) are not the a_q , but are new boson operators α_q :

$$\alpha_q = u_q a_q + v_q a_{-q}^\dagger; |u_q|^2 - |v_q|^2 = 1. \quad (5)$$

From equations (3);

$$u_q = \frac{1}{2} \left(\sqrt{\frac{\omega_q}{\epsilon_q}} + \sqrt{\frac{\epsilon_q}{\omega_q}} \right); v_q = \frac{1}{2} \left(\sqrt{\frac{\omega_q}{\epsilon_q}} - \sqrt{\frac{\epsilon_q}{\omega_q}} \right). \quad (6)$$

The magnetization is calculated by writing the expression

$$S_i^z \approx S - \frac{1}{N} \sum_q a_q^\dagger a_q, \quad (7)$$

in terms of the α operators

$$S_i^z \approx S - \frac{1}{N} \sum_q (|u_q|^2 \alpha_q^\dagger \alpha_q + |v_q|^2 \alpha_q \alpha_q^\dagger) \\ + \text{off diagonal terms} \quad (8)$$

and averaging, using the Planck function:

$$\langle S_i^z \rangle \approx S - \frac{1}{N} \sum_q \frac{\epsilon_q - \omega_q + A'/2}{2\omega_q} \\ - \frac{1}{N} \sum_q \frac{\epsilon_q + A'/2}{\omega_q} \frac{1}{\exp(\hbar\omega_q/kT) - 1}. \quad (9)$$

Equation (9) shows that this model exhibits a zero point demagnetization. The analysis given above is valid only if this demagnetization, as well as the temperature dependent demagnetization, is small compared to S . This condition places a limit on the allowed magnitude of A' .

Note added in proof: G. F. Reiter [Thesis, Stanford University, 1968, Unpublished] has also given a correct method for treating single ion anisotropy terms.

Department of Physics,
University of California,
San Diego,
La Jolla,
Calif. 92037, U.S.A.

D. R. FREDKIN
H. B. SHORE

REFERENCES

1. LIEBERMANN L. N., FREDKIN D. R. and SHORE H. B., *Phys. Rev. Lett.* **22**, 539 (1969).
2. WALKER L. R., *Magnetism* (Edited by G. T. Rado and H. Suhl), Vol. 1, p. 299. Academic Press, New York, (1963).
3. HOLSTEIN T. and PRIMAKOFF H., *Phys. Rev.* **58**, 1098 (1940).
4. BOGOLYUBOV N. N. and TYABLIKOV S. V., *Dokl. akad. Nauk SSSR* **126**, 53 (1959) — English Transl.: *Soviet Phys.-Dokl.* **4**, 604 (1959). TYABLIKOV S. V., *Ukr. Mat. Zh.* **11**, 287 (1959).
5. MARSHALL W. and MURRAY G., *J. appl. Phys.* **39**, 380; AERE-R4879, and to be published (1968)

J. Phys. Chem. Solids Vol. 31, pp. 2161–2165.

The effect of localized surface changes on transport current distributions in plates of type I superconductors*

(Received 18 September 1969)

ETCHING and sanding localized regions of the surfaces of plates of type I superconductors cause large differences in both the supercurrent distributions and the intermediate state currents when transport currents are

applied. The results are similar to the data obtained from magnetization measurements of hollow cylinders which show that the supercurrent distributions are affected by localized changes in surface properties.

The London treatment of the transport current in a plate of a type I superconductor requires that the supercurrent distribution is uniform in the zero resistance region[1]. Magnetization measurements of hollow cylinders of type I superconductors show that the induced persistent current distribution is dependent on localized surface conditions and also depends upon wall thickness[2]. In this work we report similar effects in transport current measurements in plates of type I superconductors.

Supercurrent distributions produced by transport currents were measured in the type of samples and apparatus illustrated in Fig. 1. The samples were plates of 99.999% Pb and Sn of uniform thickness cut in the symmetrical geometry shown in Fig. 1(a). The distribution of currents in the arms of the sample was determined by forming the geometry shown in Fig. 1(b) and measuring the fields generated in the loops when current flows. The arms were spaced sufficiently far apart so that no field interactions occurred. The results obtained were reproducible and independent of the width of the current leads when they exceed the arm width. The results are also independent of the spacing between the arms when the spacing is sufficiently large so that the field between the arms was zero. The type of probes used, and the precision and reproducibility associated with the equipment and techniques was described elsewhere[2]. Annealing procedures and the various methods for producing surface strains and removing surface strains through chemical etching were also described[2]. Previous work on hollow cylinders[2] showed that surfaces in which the strains were minimal carried small currents. The largest supercurrents flow in regions associated with surface strains. The transport current samples

*This work was performed under the auspices of the U.S. Atomic Energy Commission.

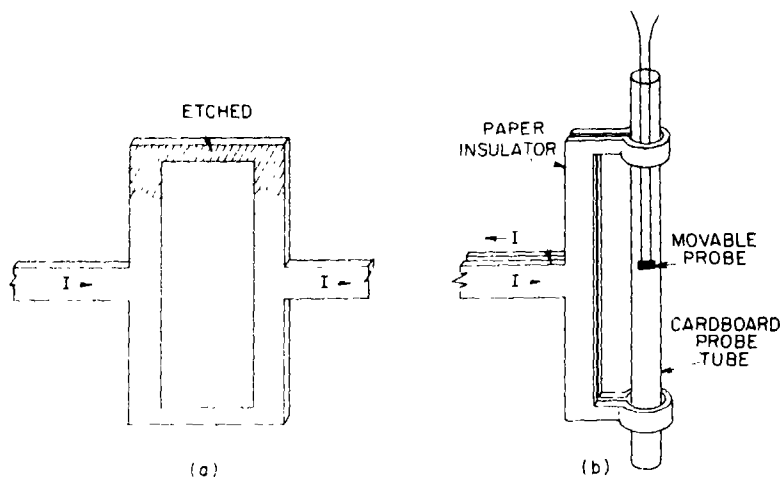


Fig. 1 Sample shape and geometry used to measure transport current distributions resulting from etched and strained surfaces

were uniformly surface strained by sanding initially. A portion of one arm was then etched to remove the surface strains as denoted in Fig. 1(a). To make certain that no appreciable differences in inductance or geometry existed between the two loops, after the measurements were completed, the etched arm was strained and the strained arm was etched. The results obtained by alternating the strained and strain-free arms were the same to within experimental error. The symmetry of the samples with respect to inductance difference was also confirmed from experiments which showed that both arms produced equal fields with current in the normal state. The data obtained from measurements of a 15 mil thick plate of 99.999% Pb at 4.2°K where the width of the arms was 150 mils are shown in Fig. 2. It is only necessary to consider the lower curve. The upper curve can be obtained from the lower curve through considerations of conservation of current and field with the experimentally confirmed information that for both arms $\Sigma \Delta H / \Delta I = \text{constant}$. The effects described here have been observed in Pb and Sn at different temperatures and appear to be characteristic of type I materials. The data represent the limiting

distributions after repeated etching and straining for a constant final thickness. Almost identical curves were obtained from different samples which were etched and sanded till the thickness reached a given value.

All portions of the curves between points 1 and 2 are reversible when I does not exceed the abscissa value of point 2. The portions of the curves between point 4 and the normal state are essentially reversible. Hysteresis first occurs when I is reduced after exceeding point 2. A typical hysteretic path associated with a point within the transition region is shown by $3 \rightarrow 6$. The sequence used to obtain the state was $1 \rightarrow 2 \rightarrow 3 \rightarrow 6$. At I applied = 0 a persistent current of the magnitude shown is created. The maximum persistent current obtained for samples with this surface to volume ratio is shown by the path $5 \rightarrow 7$. The value is less than the vertical height of the plateau. Figure 3 gives similar measurements in a 9 mil plate of otherwise identical geometry. In this case the maximum persistent current achieved is equal to the plateau height. The plateau heights are in direct ratio with the surface to volume ratio in these and all other plates studied (4–30 mils). The reverse curve and subsequent curves obtained by

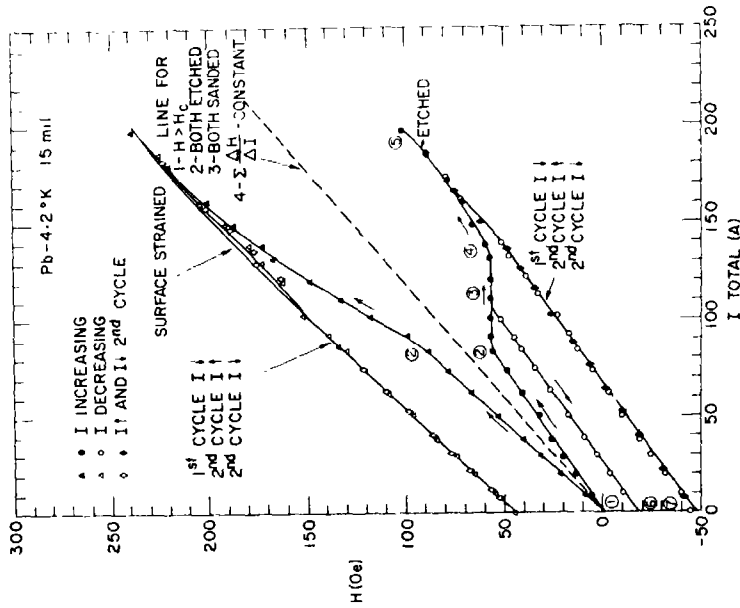


Fig 2. Supercurrent distributions resulting from a distribution in surface energy in a 15 mil thick plate of Pb at 4.2°K for various conditions of increasing and decreasing transport currents.

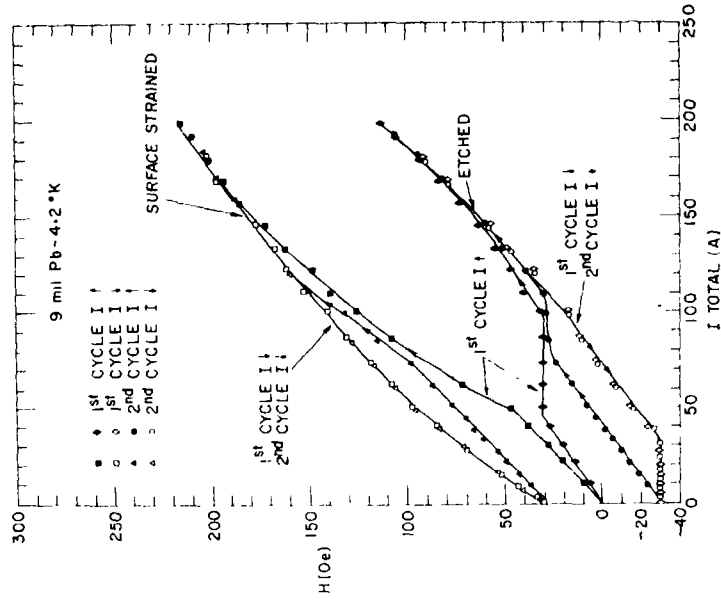


Fig. 3. Supercurrent distributions resulting from a distribution in surface energy in a 9 mil thick plate of Pb at 4.2°K for various conditions of increasing and decreasing transport currents.

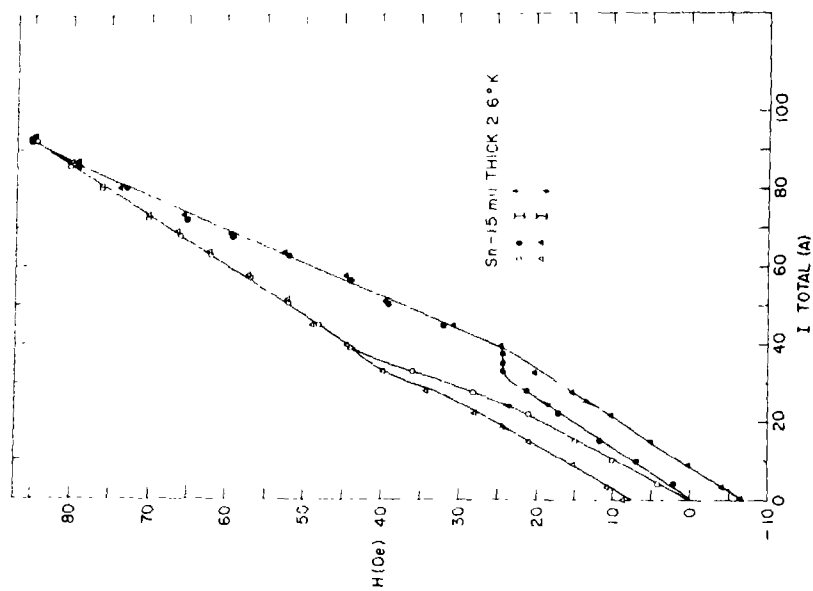


Fig. 4. Supercurrent distributions resulting from a distribution in surface energy for a 15 mil thick plate of Sn at 2.6°K. Data given for the increasing and decreasing transport currents between the superconducting and normal states.

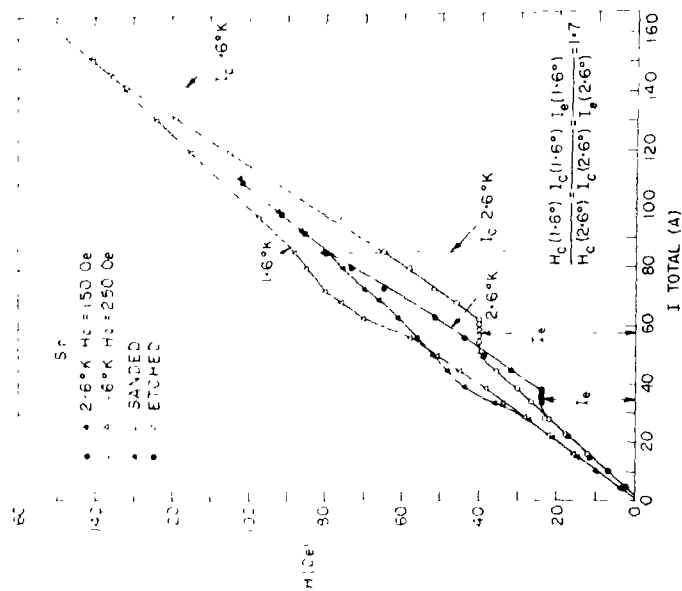


Fig. 5. Supercurrent distributions resulting from a distribution in surface energy for a 15 mil plate of Sn at two temperatures.

increasing and decreasing the applied current show changes analogous to the hysteresis observed in magnetization measurements[2]. The assumption that a difference in transport current in the two arms is sufficient to create a persistent current when the applied current is removed is not supported by the reversibility observed for the curves between points 1 and 2 in Fig. 2. The larger current may collapse into the arm carrying the smaller current and generate a persistent current in the plane of the sample when 1 applied is removed. This would create a field of opposite sense to the field observed with applied current in the etched arm in agreement with the data. Nevertheless such a current is not created by the difference associated with the region between points 1 and 2. The data show that the persistent currents are associated with the plateau region which is the only irreversible portion of the curve. Figure 4 shows the complete forward and reverse curves between the superconducting and normal state for a 15 mil plate of 99.999% Sn at 2.6°K. Data showing that the critical currents and plateau heights have the same temperature dependence as the critical fields are given in Fig. 5 for a 15 mil plate of Sn. Thinner plates of Sn show changes similar to those observed in the thinner plates of Pb. The sample shapes and equipment used for these measurements were not suitable for precise resistivity measurements. However, some qualitative conclusions can be inferred. The magnitude of the persistent currents obtained when the transport current is removed and the manner in which they are created indicate that the intermediate state first forms at currents greater than those associated with the plateau. In addition the data show that the resistivity in each arm is different and only becomes the same in the normal state.

Although the effects reported here may be minimized in solenoids due to field interactions, the results imply that localized surface effects may contribute to non-uniform

eddy currents and non-uniform dissipation in superconductors which carry an appreciable fraction of the current in the surface.

Brookhaven National
Laboratory,
Upton,
N.Y. 11973,
U.S.A.

D. G. SCHWEITZER
P. D. ADAMS

REFERENCES

1. LONDON F., *Superfluids*, Vol. 1, Dover (1960).
2. SCHWEITZER D. G., *Phys. Rev.* 173, 461-472 (1968).

J. Phys. Chem. Solids Vol. 31, pp. 2165-2167.

Cation distributions in ferrimagnetic garnets

(Received 12 September 1969)

IN RELATION with problems concerning crystal chemistry and magnetic properties of rare-earth iron garnets, Geller *et al.*[1-3], Tauber *et al.*[4] and Bozorth *et al.*[5] have investigated the distribution of cations in a crystal belonging to the system $Y_3Fe_2Fe_3O_{12} - Ca_3Fe_2M_3O_{12}$ ($M = Si, Ge, Sn$). Their results have indicated that, among non-magnetic tetravalent ions, most of those with large ionic radius such as Sn^{4+} occupy the octahedral sites in garnet, while only a small portion of ions whose radius is fairly small such as Si^{4+} or Ge^{4+} enters into the tetrahedral sites. During a study on polymorphic form of YIG[6], we have worked on the distribution of Ge^{4+} ion in a crystal belonging to the system of YIG and germanate andradite ($Ca_3Fe_2Ge_3O_{12}$).

In the preparation of starting materials with chemical composition of $(Y_{3-x}Ca_x)(Fe_{5-x}Ge_x)O_{12}$, where $x = 0, 0.5, 1.0, 1.5, 2.0, 2.5$ and 3.0 , the calculated amounts of standardized solutions of $Fe(NO_3)_3$ and $Ca(NO_3)_2$ and powders of Y_2O_3 and GeO_2 were mixed, dried, and fired until the nitrates were completely decomposed. They were then

heated at 1200°C in air for 24 hr in an electric furnace and quenched to room temperature. Then the samples were reground and refired under the same conditions.

The X-ray diffraction patterns of the baked samples were completely indexed as the garnet-type structure and this fact made it possible to calculate a change of lattice parameter with the change of the mole fraction x . As shown in Table 1, the lattice parameters decrease almost linearly with the increase of x , indicating that the complete solid solution is formed in the whole range of this system.

Table 1. Results of X-ray analysis and magnetic measurements

x	a_0 (Å)	T_c (°K)	σ_0 (erg/g) extrapolated to 0 K
0	12.380	563	5.0
0.5	12.373	478	2.6
1.0	12.361	393	1.4
1.5	12.351	353	0.7
2.0	12.340		
2.5	12.328		
3.0	12.316		

Paramagnetics in temperature range down to 80°K.

Table 2. Cation distribution in garnet analyzed from the results of magnetic measurements and Mossbauer spectra. The cations parenthesized by {}, [], and () indicate that they occupy the dodecahedral, octahedral and tetrahedral sites, respectively

x	Magnetic measurement	Mossbauer spectrum
0	{Y ₁ }[Fe ₂](Fe ₁)O ₁₂	{Y ₁ }[Fe ₁](Fe ₂)O ₁₂
0.5	{Y ₁ }[Fe _{1.96} Ge _{0.01}](Fe _{2.51} Ge _{0.19})O ₁₂	{Y ₁ }[Fe _{1.96} Ge _{0.02}](Fe _{2.52} Ge _{0.18})O ₁₂
1.0	{Y ₁ }[Fe _{1.86} Ge _{0.11}](Fe _{2.11} Ge _{0.80})O ₁₂	{Y ₁ }[Fe _{1.80} Ge _{0.20}](Fe _{2.20} Ge _{0.80})O ₁₂

Dependencies of the magnetic moment on temperature and the value of spontaneous magnetization were measured in a magnetic field up to 8000 oer. They are also tabulated in Table 1.

From these results of the magnetic measurements, the distribution of cations in the

products were calculated by following the way introduced by Gilleo *et al.*[7], and the results for $x = 0, 0.5$ and 1.0 are shown in Table 2.

Analyses of Mössbauer spectra of the samples were undertaken to examine the above-proposed cation distributions. The spectra were recorded at room temperature using the radiation from ^{57}Co in Cu with a 400 channel multichannel analyzer. The velocity was calibrated by the spectrum of $\alpha\text{-Fe}_2\text{O}_3$ and also by that of stainless steel. The analysis itself is principally based on the method by which Bowen *et al.*[8] obtained the ratio of Fe^{2+} to Fe^{3+} in mica. The area of an absorption line which corresponds to a certain velocity is proportional to the number of the absorbing nuclei (^{57}Fe) per unit area in the absorber. If the absorber contains more than one distinguishable site for iron, the comparison of intensity of each peak in a spectrum gives us an information on the relative population of iron atoms in a sample. The cation distributions calculated in this way are listed in Table 2. The noticeable consistency with the results of magnetic measurements is seen in this table. For $x = 1.0$, the present result also shows a

good agreement with that reported by Bozorth *et al.*[5].

College of General Education and
Institute of Scientific and Industrial Research,
Osaka University, Osaka, Japan

M. SHIMADA
S. KUME
M. KOIZUMI

REFERENCES

1. GELLER S. and GILLES M. A., *J. Phys. Chem. Solids* **3**, 30 (1957).
2. GELLER S., BOZORTH R. M., GILLES M. A. and MILLER C. E., *J. Phys. Chem. Solids* **12**, 111 (1959).
3. GELLER S. and MILLER C. E., *Acta. crystallogr.* **13**, 179 (1960).
4. TAUBER A. and KEDESZY H. H., *J. appl. Phys.* **29**, 385 (1958).
5. BOZORTH R. M. and GELLER S., *J. Phys. Chem. Solids* **11**, 263 (1959).
6. SHIMADA M., KUME S. and KOIZUMI M., *J. Amer. Cer. Soc.* **51**, 713 (1968).
7. GILLES M. A. and GELLER S., *Phys. Rev.* **110**, 73 (1958).
8. BOWEN L. H., WEED S. B. and STEVENS J. G., *Amer. Mineral.* **54**, 72 (1969).

J. Phys. Chem. Solids Vol 31, pp 2167-2169.

Valence band of thallium selenide

(Received 29 April 1969)

IN A PREVIOUS publication[1] the results of measurement of electrical conductivity and thermoelectric power of lead-doped thallium selenide had been reported. It has been found that these results could be qualitatively explained on the basis of a two valence band semiconductor. In this note the results of the calculations made to obtain the separation between the two valence bands are presented.

Figure 1 shows the experimental results (solid curve) obtained from the doping investigation with thermoelectric power (α) plotted as a function of electrical conductivity (σ). Here only that portion of the curve which corresponds to the appreciable contribution from both bands are presented.

Before the equations can be written for the thermoelectric power (α) and electrical conductivity (σ) for a two valence band semiconductor, it is assumed that both bands are spherical and that the carriers undergo acoustic scattering. For a semiconductor in which two valence bands are to be considered, the thermoelectric power and the

electrical conductivity are given by [2]

$$\alpha = (\alpha_L \sigma_L + \alpha_U \sigma_U) / \sigma_L + \sigma_U$$

$$\sigma = \sigma_L + \sigma_U$$

where L and U refer to the lower and upper energy bands, respectively. However, for acoustics scattering α_L and α_U are given by [2]

$$\alpha_L = (k/e) \left[\frac{2F_1(\eta)}{F_0(\eta)} - \eta \right]$$

$$\alpha_U = (k/e) \left[\frac{2F_1(\eta - \Delta)}{F_0(\eta - \Delta)} - (\eta - \Delta) \right]$$

where $F_r(\eta)$'s are Fermi integrals[3] defined by

$$F_r(\eta) = \int_0^\infty \frac{x^r dx}{1 + \exp(x - \eta)}$$

η is the reduced Fermi energy

$$\eta = (\epsilon_f - \epsilon_L) / kT$$

and Δ is the reduced energy difference between the two bands,

$$\Delta = (\epsilon_U - \epsilon_L) / kT.$$

The electrical conductivities σ_L and σ_U are given by [2]

$$\sigma_L = 2e(2\pi mkT/h^2)^{3/2} F_0(\eta) \mu_L (m_L^*/m)^{3/2}$$

$$\sigma_U = 2e(2\pi mkT/h^2)^{3/2} F_0(\eta - \Delta) \mu_U (m_U^*/m)^{3/2}$$

where m^* is the effective mass of holes and μ is the mobility. In order to obtain a correspondence between the experimental and theoretical values, it is necessary to vary the parameters $\mu_L(m_L^*/m)^{3/2}$, $\mu_U(m_U^*/m)^{3/2}$ and Δ in such a way that suitable values are obtained. This is achieved as follows. The parameters $\mu_L(m_L^*/m)^{3/2}$, $\mu_U(m_U^*/m)^{3/2}$ and Δ were so chosen as to obtain two curves on either side of the experimental curve.

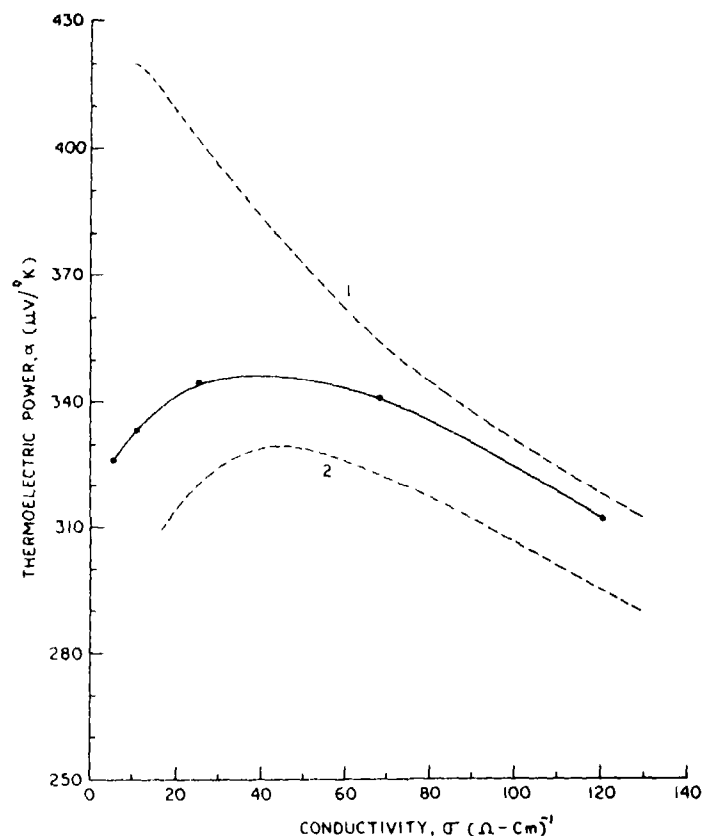


Fig. 1 Thermoelectric power as a function of electrical conductivity. Solid curve is the experimental results and the dotted curves are the theoretical values calculated according to the two valence band model.

Two such curves (1 and 2) are shown in Fig. 1. This procedure determines the ranges of $\mu_i(m_i^*/m)^{3/2}$ and $\mu_v(m_i^*/m)^{3/2}$ for a fixed value of $\Delta \approx 8$. Finally a computer program was written and these parameters were accurately determined so that the theoretical $\alpha = f(\sigma)$ curve lies on the experimental curve. Best correspondence between experimental and theoretical curves was obtained with the following parameters

$$\Delta = 7.9$$

$$\mu_i(m_i^*/m)^{3/2} = 2.65 \times 10^{-5} \text{ cm}^2(\text{V Sec})^{-1}$$

$$\mu_v(m_i^*/m)^{3/2} = 8.95 \times 10^{-3} \text{ cm}^2(\text{V Sec})^{-1}.$$

Since Δ is known the separation between the two valence bands was calculated and comes out to be 0.197 eV. This is about 1/3 of the energy band gap of thallium selenide [4] which is 0.574 eV.

Acknowledgements—It is a pleasure to thank Professor B. D. Nagchaudhuri for his valuable suggestions. The author is thankful to Dr. C. S. Shastry, presently Department of Physics, Louisiana State University, U.S.A., for his help in writing a computer program.

Saha Institute of Nuclear Physics,
Calcutta-9,
India

P. S. NAYAR

REFERENCES

1. NAYAR P. S., VERMA J. K. D. and NAG B. D.,
J. appl. Phys. **40**, 123 (1969).
2. RONNLUND B., BECKMAN O. and LEVY H.,
J. Phys. Chem. Solids **26**, 1266 (1965).
3. BLAKEMORE J. S., *Semiconductor Statistics*.
Pergamon Press, Oxford (1962).
4. NAYAR P. S., VERMA J. K. D. and NAG B. D.,
J. phys. Soc. Japan **23**, 144 (1967).

DIRECTIONAL DISPERSION OF EXTRAORDINARY OPTICAL PHONONS IN α -QUARTZ IN THE FREQUENCY DOMAIN FROM 380 TO 640 cm^{-1}

J. ONSTOTT

Case-Western Reserve University, Cleveland, Ohio 44106, U.S.A.

and

G. LUCOVSKY

Xerox Corporation, Rochester, N.Y. 14604, U.S.A.

(Received 24 November 1969; in revised form 23 January 1970)

Abstract—The room temperature i.r. reflectivity of α -quartz was measured in the spectral range from 380 to 640 cm^{-1} . Reflectivity at normal incidence was studied as a function of the angle between the c-axis and the crystal surface in a geometry in which the polarization vector of the incident light, the c-axis, and propagation vector were coplanar. This is the geometry in which coupling to extraordinary optical phonons occurs. Reflectivity spectra were analyzed using a Kramers-Kronig dispersion analysis and a classical harmonic oscillator formalism. The directional dispersion of the i.r. extraordinary phonon modes in α -quartz was calculated using a coupled harmonic oscillator formalism. The experimental frequencies of the coupled modes were in excellent agreement with the results of this calculation.

1. INTRODUCTION

THE INFRARED spectrum of α -quartz has been studied extensively [1-3]. Recently, the use of laser Raman spectroscopy [4] has helped to complete the assignment of the frequencies and symmetry character of the fundamental optical phonon modes at the center of the Brillouin zone. In α -quartz, there are 9 atoms per unit cell, hence 27 degrees of freedom. Subtracting the three acoustical phonon branches, there are 24 optical phonon branches. Their number, activity, degeneracy, and symmetry character at the zone center are:

4 Raman-active, i.r.-inactive, nondegenerate phonons of A_1 character

4 i.r.-active, Raman-inactive, nondegenerate phonons of A_2 character

8 i.r.-active, Raman-active, doubly degenerate phonons of E character.

The i.r.-active modes are split by electrostatic forces into transverse and longitudinal components.

Since α -quartz is a uniaxial crystal, there is

a directional dispersion in the i.r.-active phonon frequencies in the extraordinary ray geometry [5]. Merton [6] has calculated this for α -quartz using a dielectric constant formalism [5]. Lucovsky, Burstein, and Pinzcuk [7] have used a phenomenological equation-of-motion formalism to generate a similar result. Their formalism, in addition to providing a simpler procedure for generating the matrix from which the frequencies and coordinates of the mixed modes are obtained also provides additional insight into the mode coupling mechanism. Their phenomenological interpolation scheme is used by us.

There have been several experimental studies of mixed modes in α -quartz. Mathieu *et al.* [8] used Raman spectroscopy to study the $E(t) - E(1)$ branch near 400 cm^{-1} , the $E(t) - E(1)$ branch near 800 cm^{-1} and $A_2(1) - E(1)$ branch near 1235 cm^{-1} . Their measurements were restricted, however, to three directions of propagation: 0°, 45° and 90° to the c-axis. Coutre-Mathieu *et al.* [9] used Raman

spectroscopy to study the $E(t) - E(1)$ branch near 800 cm^{-1} and i.r. spectroscopy to study the $A_2(t) - A_2(1)$ branch just below 800 cm^{-1} . Scott and Porto[4], Loudon[10], and Scott [11] have also studied this effect in α -quartz using laser Raman spectroscopy.

Here we report the first study by i.r. spectroscopy of modes near 475 cm^{-1} with $A_2(t) - E(t)$ and $E(1) - A_2(1)$ character[12]. There are several motivations for this study. It represents a case where electrostatic splitting is dominant over anisotropy splitting. Previous studies using i.r.-spectroscopy have been restricted to anisotropy split bands[6]. Further, our i.r. studies show that fine structure observed by Spitzer and Kleinman[3] in the A_2 mode of this pair results from mode coupling.

In Section 2 we discuss the experimental procedures and in Section 3 the experimental results. Section 4 treats the analysis of the reflectivity spectra using Kramer-Kronig and harmonic oscillator formalisms. Section 5 discusses the phenomenological theory of directional dispersion. Section 6 compares the experimental results with theoretical curves as computed in this paper.

2. EXPERIMENTAL PROCEDURES

Ten synthetic crystals of α -quartz, obtained from Valpey Corporation, optically polished on one side only, and cut so that the c -axis made angles between 0 - 90° with the polished surface were used in the measurements. Reflectance measurements were made at ambient temperatures, at near normal incidence (9°), using a Perkin-Elmer 301 Spectrometer. Measurements were made in the spectral region from 380 to 640 cm^{-1} using a 40 line/mm grating in first order. The mechanical slit width was 0.5 mm which gives a spectral slit width of about 4 cm^{-1} . A AgBr wire grid polarizer was used; the direction of polarization was perpendicular to the plane of incidence, and the samples were oriented so that the projection of the c -axis on the polished face was parallel to the polarization (see Fig. 1 insert). The reflectance of the quartz samples

was normalized by comparison with that of a front surface aluminum mirror.

3. EXPERIMENTAL RESULTS

Figures 1(a) and 1(b) contain the measured reflectance of the ten samples of α -quartz. For the 0 and 90° samples, the reflectivity is essentially the same as that measured by Spitzer and Kleinman[3]; however, we find no fine structure in the 0° data. At intermediate angles except for 80° , there is structure indicative of at least two modes. Note further that the effects of mode coupling are much more pronounced in the reflectivity for angles close to 0° as compared to angles close to 90° . The structure near 400 cm^{-1} is due to an $E(1) - E(t)$ mode and is not emphasized in this study. In the $E||c$ spectrum of Spitzer and Kleinman [3], there is a dip in the reflectivity at approximately 500 cm^{-1} . Comparison of these data with our data for $\theta = 10^\circ$ suggests that the observed dip results from mode coupling caused either by a slight crystal misalignment (i.e. between the c -axis and surface) or by surface damage. Directional dispersion is favored in this orientation due to the parallel alignment of the polarization and the c -axis, or in the case of a slightly misaligned or damaged sample, its projection on the sample surface. The absence of this dip in our results rules out some other explanations for its possible occurrence in the other study, e.g. a forbidden mode being made active by a relaxation of symmetry selection rules at an ideal surface. Scott and Porto[4] had come to a similar conclusion regarding this fine structure using Raman spectroscopy.

4. ANALYTICAL ANALYSIS OF EXPERIMENTAL DATA

A two step procedure was used to obtain the mode frequencies from the experimental reflectivity. Approximate frequencies of the phonon modes were obtained using a Kramers-Kronig ($K-K$) dispersion analysis. These, along with mode strength and damping parameters, were used in a harmonic oscillator

formalism to synthesize the reflectivity. The parameters of the phonon harmonic oscillators were adjusted until an optimum fit between the synthesized and experimental reflectivity was obtained.

The K - K analysis is an integral relationship between the real and imaginary parts of any one of the linear frequency dependent response

functions used to characterize the medium. In our analysis these are the real and imaginary parts of the complex dielectric constant, ϵ_1 and ϵ_2 , respectively. In order to use this transform technique, it is necessary to know the value of the reflectivity in all of frequency space. In experiments this is not available and an analytical extrapolation procedure must be

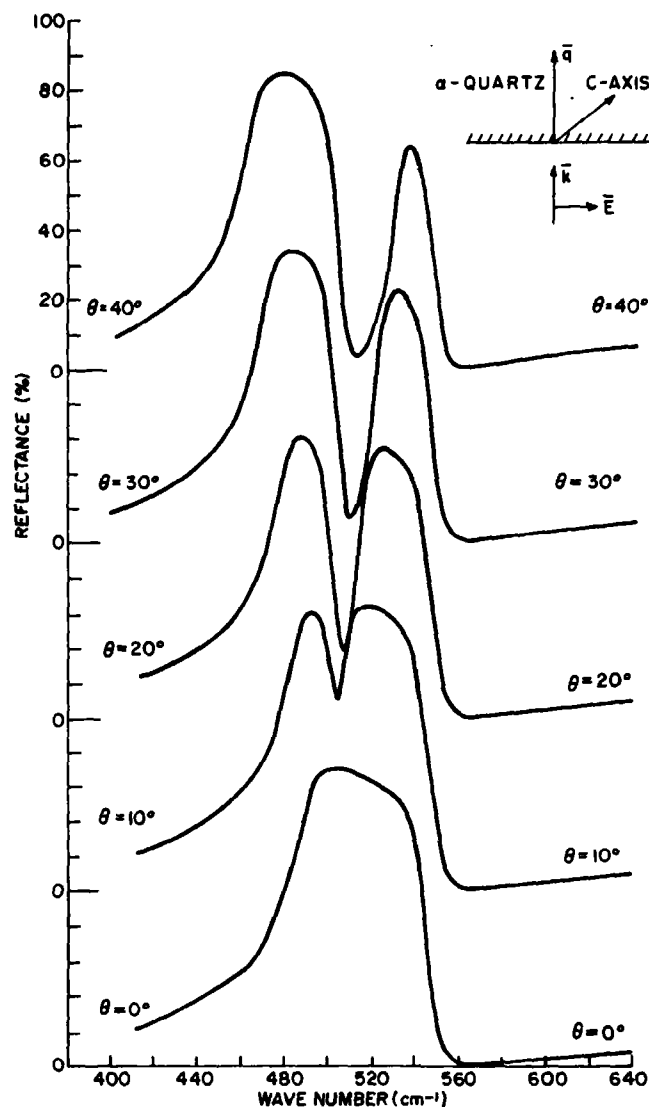


Fig. 1(a).

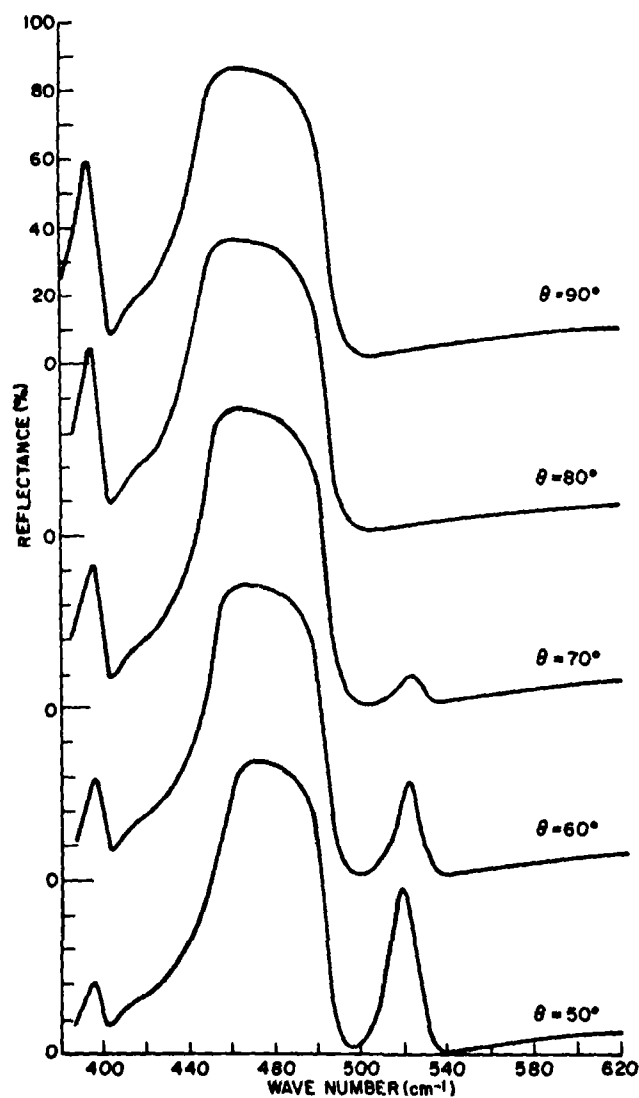


Fig. 1(b)

Fig. 1. The reflectivity of α -quartz in the extraordinary ray geometry as a function of θ , the angle between the c -axis and crystal surface. 1(a) contains the spectra for $\theta = 0, 10, 20, 30$ and 40° , 1(b) for $\theta = 50, 60, 70, 80$ and 90° . The insert shows the sample geometry for this experiment.

applied to the reflectivity to extend it to both low and high frequencies. This extrapolation limits the accuracy of the mode parameters obtained from this analysis, i.e. the resonant

frequencies, ω_{Ti} , the mode strengths, $4\pi\rho_i$, and the damping constants, γ_i .

Our measurements were restricted to the range from 380 to 640 cm^{-1} . However, the

modes were sufficiently strong and sufficiently isolated in frequency that we were able to approximate the reflectivity at low and high frequencies by a constant value and obtain a good set of mode parameters. This follows because the largest contributions to complex dielectric constant come from regions where the reflectivity changes rapidly. Contributions from other modes are diminished as they become displaced from the domain of interest. In the analytical procedure we employ, the pair of response function variables are the magnitude of the reflectivity R and complex phase θ . The phase angle is calculated from the experimental reflectivity using the equation

$$\theta(\omega) = \frac{1}{2\pi} \int_0^\infty \frac{d \ln R}{d\omega'} \ln \left| \frac{\omega' + \omega}{\omega' - \omega} \right| d\omega'. \quad (1)$$

The complex dielectric constant is then obtained from the computed values of $\theta(\omega)$ and from the experimental reflectivity $R(\omega)$.

Figure 2 contains the frequency dependence of the dispersion parameters ϵ_2 and the energy loss term, $-Im(1/\epsilon)$ as obtained from the K - K analysis for one of the samples. The structure in these parameters is sharp, and approximate mode parameters are readily obtained. The transverse frequencies, ω_{Ti} , are

obtained from the positions of the maxima in ϵ_2 . The damping parameters, γ_i , are estimated from the half-widths the ϵ_2 peaks. The oscillator strengths, $4\pi\rho_i$, are approximated from the maximum values of the peaks in ϵ_2 and their half widths, i.e.

$$4\pi\rho_i \approx (\epsilon_2)^{\max} \gamma_i. \quad (2)$$

The parameters from the K - K analysis are then used in a Lorentzian harmonic oscillator formalism to create a synthetic reflectivity spectrum. For an assembly of oscillators,

$$\epsilon_1 = \epsilon_0 + \sum_i \frac{4\pi\rho_i \omega_{Ti}^2 (\omega_{Ti}^2 - \omega^2)}{(\omega_{Ti}^2 - \omega^2)^2 + \gamma_i^2 \omega_{Ti}^2 \omega^2}, \quad (3)$$

and

$$\epsilon_2 = \sum_i \frac{4\pi\rho_i \omega_{Ti}^2 \gamma_i \omega \omega_{Ti}}{(\omega_{Ti}^2 - \omega^2)^2 + \gamma_i^2 \omega_{Ti}^2 \omega^2}, \quad (4)$$

where ϵ_0 is the high frequency dielectric constant. ϵ_0 is obtained from the results of Spitzer and Kleinman[3] and is equal to the sum of the dielectric constants due to electronic transitions and to those phonon modes with resonant frequencies higher than the modes being studied. The reflectivity is calculated in the usual way:

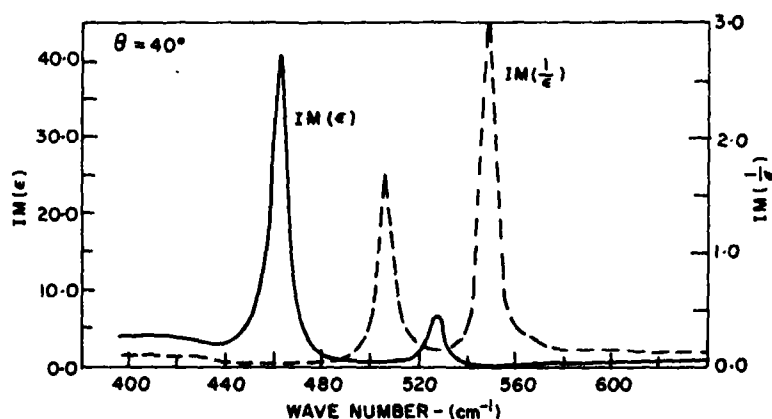


Fig. 2. The imaginary (ϵ_2) parts of the dielectric constant and the energy loss term ($-Im(1/\epsilon)$) as a function of frequency for the $\theta = 40^\circ$ sample as obtained from the K - K analysis.

$$R = \left| \frac{\sqrt{\epsilon} - 1}{\sqrt{\epsilon} + 1} \right|^2 \quad (5)$$

Figure 3 contains a comparison of the experimental reflectivity and the synthesized spectrum for one of the samples. The fit is excellent in the vicinity of the reststrahlen structure, but systematic deviations occur at both high and low frequencies due to the neglect of other phonon modes.

Table 1 contains the oscillator parameters obtained from the above procedure. Included also are the values of the longitudinal modes.

The transverse mode frequencies show a strong directional dispersion, but the longitudinal mode frequencies are essentially the same at all angles. Figure 4 contains a plot of the transverse frequencies ω^+ and ω^- as a function of angle. This will be compared with the frequency dispersion obtained from the phenomenological interpolation scheme (see Section 6).

5. THEORETICAL ANALYSIS

Merten[6] has used a dielectric constant formalism[5] to calculate the directional

Table 1. Harmonic oscillator parameters of the normal modes as obtained from the best fit procedures

Angle of c-axis to surface	ω_{TO-} (cm ⁻¹)	ω_{TO+} (cm ⁻¹)	$4\pi\rho$	γ	ω_{LO-} (cm ⁻¹)	ω_{LO+} (cm ⁻¹)	$4\pi\rho_+$	γ_+
0	548	489	0.82	0.012	†	†	†	†
10	505	486	0.74	0.011	548	507	0.08	0.015
20	505	478	0.77	0.014	549	515	0.10	0.009
30	505	471	0.75	0.011	549	522	0.11	0.010
40	505	464	0.79	0.012	548	528	0.088	0.010
50	506	458	0.82	0.012	548	534	0.066	0.012
60	505	453	0.83	0.013	549	539	0.048	0.014
70	505	448	0.84	0.013	549	543	0.031	0.022
80	505	445	0.78	0.014	*	*	*	*
90	505	444	0.78	0.014	†	†	†	†

*Not observed

†Only one mode present at these angles.

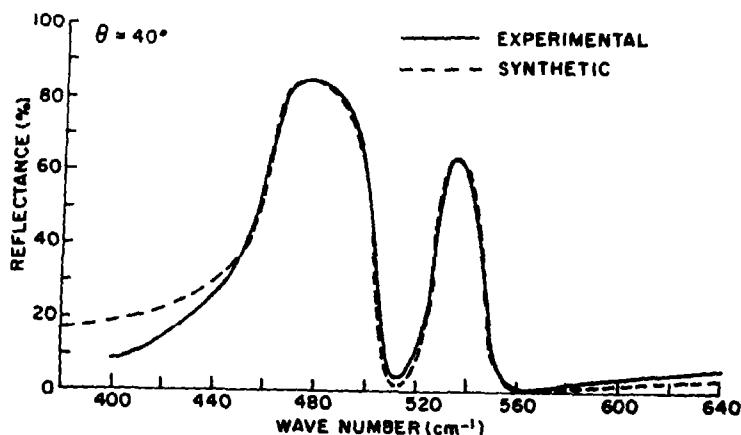


Fig. 3. Comparison of the experimental and synthesized reflectivity spectra for the $\theta = 40^\circ$ sample.

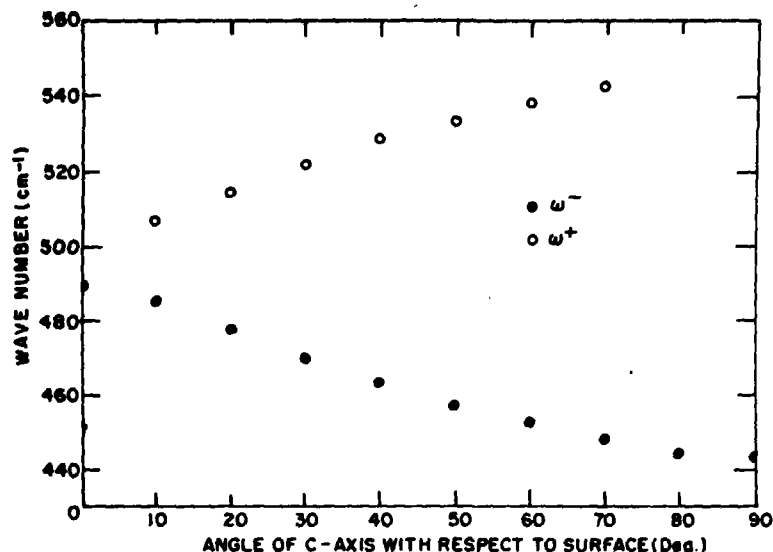


Fig. 4. Plot of the normal mode frequencies ω^+ and ω^- as a function of the angle between the c -axis and the surface.

dispersion of extraordinary phonons in α -quartz. We present an alternative calculation using a phenomenological approach based on a coupled harmonic oscillator formalism [7, 13]. The development of this procedure resulted, in part, from difficulties experienced by us in using the dielectric constant formalism with input frequencies different from Merten's [6]. Specifically, our values for the transverse E and A_2 phonons near 475 cm^{-1} are slightly lower than those used by Merten [6]; however, the discrepancy (about 1 per cent) is within our experimental resolution.

In addition to computational conveniences, other advantages realized in this alternative approach are:

- (1) the coupling mechanism that generates the new normal modes is clearly identified;
- (2) the matrix from which frequencies and coordinate vectors are derived is simply obtained from the equations of motion; and
- (3) the formalism is readily applied to other types of coupled mode behavior in anisotropic media, for example, coupled cyclotron reson-

ance-plasmon-phonon modes in polar semiconductors [7, 14].

We take advantage of the fact that phonons, in the absence of anharmonic forces, are independent of each other and have the properties of harmonic oscillators. We first consider a case of the coupling between two anisotropy-split phonon modes in a uniaxial crystal [13]. Referring to Fig. 5, we assume a single i.r.-active phonon branch for which the threefold degeneracy is split by the crystal anisotropy. We choose the Z -direction as that of the optic axis or c -axis, so that for propagation vectors parallel to Z we have no TO phonon frequency $\omega_{2T} = \omega_{TX} = \omega_{TY}$ and one LO phonon frequency $\omega_{1L} = \omega_{LZ}$. For propagation parallel to either X or Y we have two TO phonon frequencies $\omega_{2T} = \omega_{TX} = \omega_{TY}$ and $\omega_{1T} = \omega_{TZ}$, and one LO phonon frequency $\omega_{2L} = \omega_{LX} = \omega_{LY}$. X , Y and Z are the principal axes of the crystal. For propagation parallel to X or Y , the TO phonon frequencies differ depending on whether the mode displacement coordinate is directed along or perpendicular to the c -axis.

alization of the coefficient matrix of equation (9). In terms of the plasma frequencies, the longitudinal frequencies are given by

$$\begin{aligned}\omega_{1L}^2 &= \omega_{1T}^2 + \Omega_1^2, \text{ and} \\ \omega_{2L}^2 &= \omega_{2T}^2 + \Omega_2^2.\end{aligned}\quad (11)$$

We introduce two new frequency designations,

$$\begin{aligned}(\omega'_1)^2 &= \omega_{1T}^2 + \Omega_1^2 \sin^2 \theta, \\ (\omega'_2)^2 &= \omega_{2T}^2 + \Omega_2^2 \cos^2 \theta,\end{aligned}\quad (12)$$

and show that there are two types of normal mode solutions. The character of the normal modes is determined by the relative magnitudes of the respective *LO-TO* phonon frequency splittings and the anisotropy splittings.

Case (1). For the case of a large anisotropy splitting defined by

$$[(\omega'_1)^2 - (\omega'_2)^2]^2 \gg 4\Omega_1^2\Omega_2^2 \sin^2 \theta \cos^2 \theta, \quad (13)$$

the new normal mode frequencies ω_+ and ω_- are given by

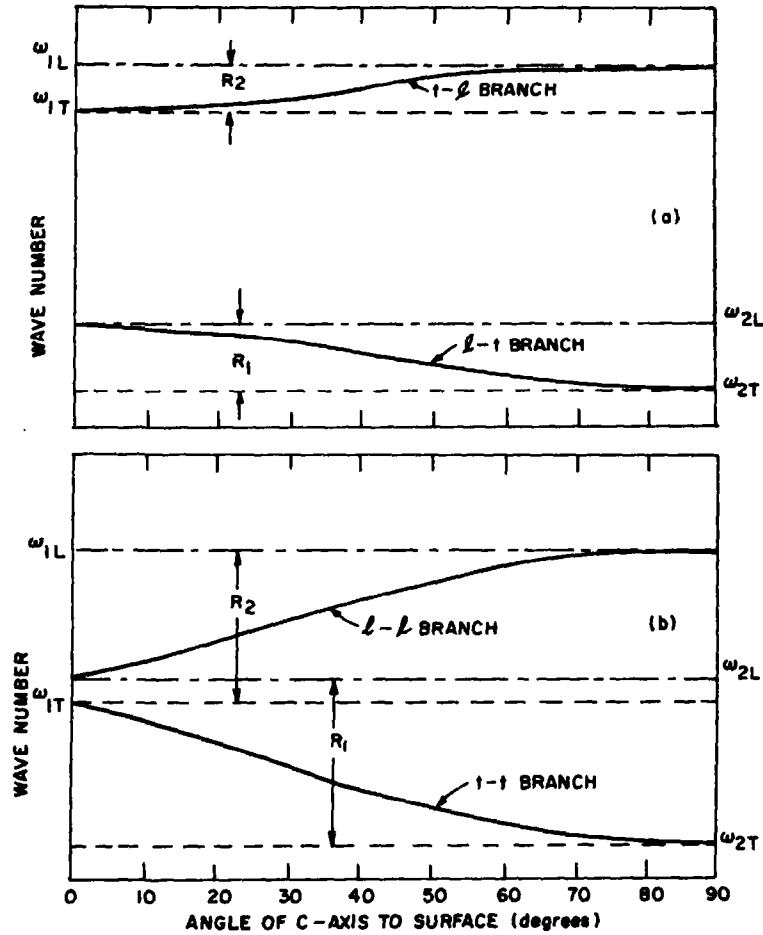


Fig. 6. (a) Calculated dispersion curves for the case of a large anisotropy splitting. (b) Calculated dispersion curves for the case of a small anisotropy splitting.

$$\begin{aligned}\omega_+^2 &= \omega_{1T}^2 \cos^2 \theta + \omega_{1L}^2 \sin^2 \theta, \text{ and} \\ \omega_-^2 &= \omega_{2T}^2 \sin^2 \theta + \omega_{2L}^2 \cos^2 \theta.\end{aligned}\quad (14)$$

We have arbitrarily set $\omega_{1T} > \omega_{2T}$. The eigenvectors are u_x and u_z and are neither transverse nor longitudinal. The mode character of ω_+ is $(t-1)$, and ω_- is $(1-t)$. The mode dispersion is pictured in Fig. 6(a). Note that the frequencies for the ω_+ branch are contained within the LO - TO phonon frequency regime of mode 1, whereas the frequencies of ω_- branch are contained within the corresponding frequency regime of mode 2.

Case (2). For the case of small anisotropy splittings, or equivalently large electrostatic LO - TO phonon frequency splittings, we have

$$\begin{aligned}\omega_+^2 &= \omega_{2L}^2 \cos^2 \theta + \omega_{1L}^2 \sin^2 \theta, \\ \omega_-^2 &= \omega_{1T}^2 \cos^2 \theta + \omega_{2T}^2 \sin^2 \theta.\end{aligned}\quad (15)$$

The eigenvectors of these modes are quasi-longitudinal and quasitransverse, respectively, with respect to the direction of propagation. Figure 6(b) displays the normal mode dispersion for this case. The mode designations, $(1-1)$ and $(t-t)$, are consistent with those defined for case (1), the ω_+ branch being contained between the principal mode LO phonon frequencies and the ω_- branch between the principal mode TO phonon frequencies.

When more than two modes are involved, the algebra is more complicated and no distinctions between large and small anisotropy splitting can be defined simply. We now apply our formalism to α -quartz to calculate the directional dispersion of that crystal. The geometry for this calculation is the same as that shown in Fig. 5; however, we have used a subscript notation which is appropriate to the symmetric character of the i.r.-active modes in α -quartz.

Phonon coordinates for which mode motion is along the c -axis are denoted by $u_{A_2}(j)$ where $j = 1, \dots, 4$, and coordinates for which mode motion is perpendicular to the c -axis are

denoted by $u_E(i)$ where $i = 1, \dots, 8$. Transverse resonant frequencies, plasma frequencies, and effective charges are also defined using the notation given above.

The coupled equations of motion are given by

$$M\ddot{u}_E(i) + M\omega_E^2(i)u_E(i) = e_E^*(i)E_M(E), \quad i = 1, \dots, 8, \quad (16)$$

and

$$M\ddot{u}_{A_2}(j) + M\omega_{A_2}^2(j)u_{A_2}(j) = e_{A_2}^*(j)E_M(A_2), \quad j = 1, \dots, 4,$$

where $E_M(E)$ and $E_M(A_2)$ are components of the macroscopic polarization field.

We have assumed equal mode masses. This assumption does not affect the calculations of normal mode frequencies and coordinates. The macroscopic field in the direction of phonon propagation is given by

$$E_M(\bar{q}) = 4\pi N \left[\sum_{j=1}^4 e_{A_2}^*(j)u_{A_2}(j) \sin \theta - \sum_{i=1}^8 e_E^*(i)u_E(i) \cos \theta \right]; \quad (17)$$

the components $E_M(E)$ and $E_M(A_2)$ are

$$\begin{aligned}E_M(E) &= E_M(\bar{q}) \cos \theta \quad \text{and} \\ E_M(A_2) &= -E_M(\bar{q}) \sin \theta.\end{aligned}\quad (18)$$

Substituting (17) and (18) into (16) and assuming sinusoidal solutions yields the equations of motion for the coupled system:

$$\begin{aligned}& [\omega_E^2(i) + \Omega_E^2(i) \cos^2 \theta - \omega^2]u_E(i) \\ & + \frac{4\pi N}{M} e_E^*(i) \sum_{k \neq i}^8 e_E^*(k)u_E(k) \cos^2 \theta \\ & - \frac{4\pi N}{M} e_E^*(i) \sum_{j=1}^4 e_{A_2}^*(j)u_{A_2}(j) \sin \theta \cos \theta = 0, \\ & i = 1, \dots, 8,\end{aligned}\quad (19a)$$

and

$$[\omega_{A_2}^2(j) + \Omega_{A_2}^2(j) \sin^2 \theta - \omega^2]u_{A_2}(j)$$

$$\begin{aligned}
& + \frac{4\pi N}{M} e_{A_2}^*(j) \sum_{l \neq j}^4 e_{A_2}^*(l) u_{A_2}(l) \sin^2 \theta \\
& - \frac{4\pi N}{M} e_{A_2}^*(j) \sum_{i=1}^8 e_E^*(i) u_E(i) \sin \theta \cos \theta = 0, \\
& j = 1, \dots, 4. \quad (19b)
\end{aligned}$$

Diagonalization of the coefficient matrix of equations (19a) and (19b) yields the normal mode frequencies and coordinates. Equations (19a) and (19b) are expressed in terms of the *TO* mode frequencies and their oscillator strengths (or plasma frequencies) analogous to equation (9). For the two mode case, one A_2 mode and one E mode, it was convenient to introduce the *LO* frequencies of the modes and to express the resultant dispersion in terms of the *TO* and *LO* frequencies of the two principal modes, i.e. equations (14) and (15). For the multimode case in α -quartz, the same procedure is not easily realized since the true longitudinal mode frequencies, as determined by the positions of the peaks in $-Im(1/\epsilon)$, are determined by the *TO* phonon frequencies and oscillator strengths of all of the modes of the system having the same symmetry character. However for computational purposes, a set of

'longitudinal' frequencies can be defined such that each of these frequencies is solely dependent on the *TO* frequency and oscillator strength of only one of the modes. If we designate these frequencies as $\omega'_{E,A_2}(L, i)$, then

$$[\omega'_{E,A_2}(L, i)]^2 = \omega_{E,A_2}^2(i) + \Omega_{E,A_2}^2(i). \quad (20)$$

These frequencies and the *TO* frequencies are then used as input for the computer diagonalization and are given in Table 2. Figure 7 indicates the directional dispersion of i.r. extraordinary phonons in α -quartz. This result is essentially the same as that derived by Merten[6], but differs only in the magnitudes of the frequencies near 475 cm^{-1} . There are 8 (*t*-1) or (1-*t*) branches, 2 (*t*-*t*) branches and 2 (1-1) branches. A comparison of the directional dispersion in the (1-1) and (*t*-*t*) branches near 475 cm^{-1} calculated using the complete set of phonon frequencies and calculated using an approximation which neglects all modes other than those involved in the coupling indicates almost identical results. Specifically, the calculated frequencies differ by at most 2 cm^{-1} (less than $\frac{1}{2}$ per cent); this is a manifestation of the isolated nature of the phonon modes being studied.

Table 2. Measured values of the *LO* and *TO* phonon frequencies of α -quartz and the input frequencies used in the harmonic oscillator formalism calculation

Mode character	Measured frequencies (cm^{-1})		Computer input frequencies (cm^{-1})	
	<i>TO</i> phonon	<i>LO</i> phonon	<i>TO</i> phonon	<i>LO</i> phonon
E	128	128	128	128
	265	265	265	265
	394	401	394	417
	444 (450)*	505 (509)†	444	520
	697	697	697	697
	795	807	795	813
	1072	1235	1072	1220
	1162	1162	1162	1162
A_2	364	386	364	412
	489 (495)*	547 (548)†	489	560
	778	790	778	794
	1080	1240	1080	1223

*Ref. [4], Scott and Porto.

†Ref. [6], Merten.

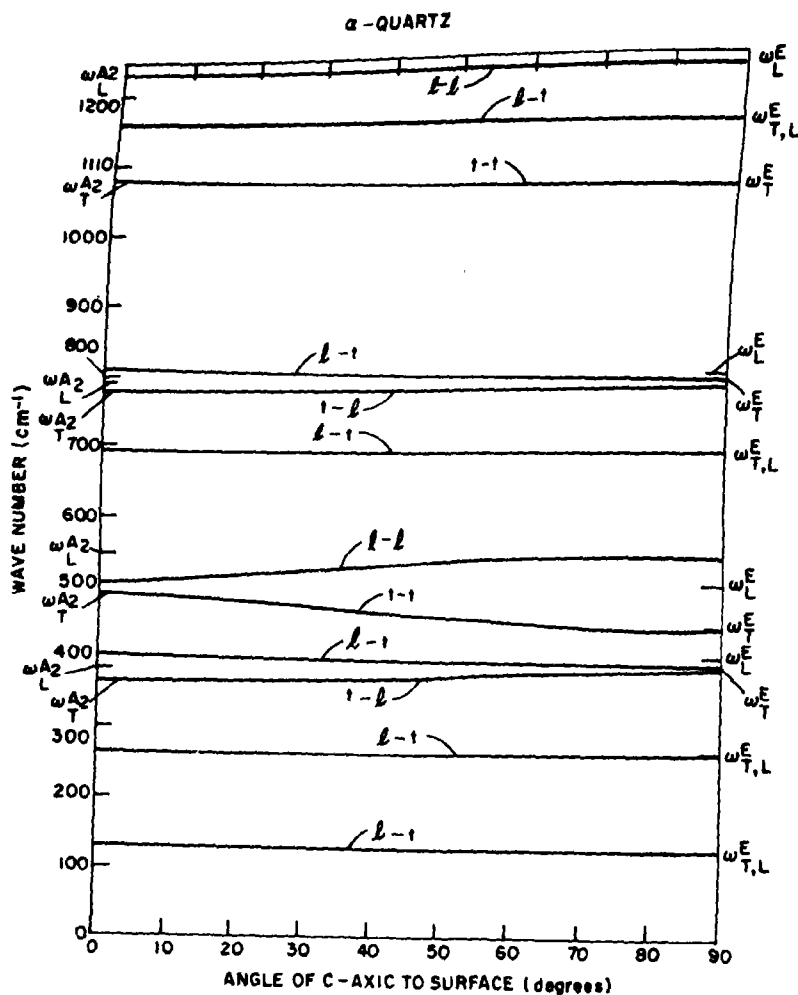


Fig. 7. Directional dispersion for extraordinary phonons in α -quartz.

6. DISCUSSION OF EXPERIMENTAL RESULTS

Figure 8 contains a comparison of the measured and calculated directional dispersion curves. The agreement is well within experimental error. Also included are points as calculated by Merten; they are displaced in frequency due to the different input frequencies used in his calculation [6]. In our calculation we have neglected mode damping in the coupled equations of motion. The neglect of this term does not influence the calculation of

normal mode frequencies if the damping is small. This is the case in α -quartz. Damping can be included phenomenologically after matrix diagonalization to generate a synthesized reflectivity spectrum. Alternatively, the reflectivity can be calculated directly using the dielectric constant formalism [15].

7. SUMMARY

We have measured the room temperature i.r. reflectivity in α -quartz as a function of the

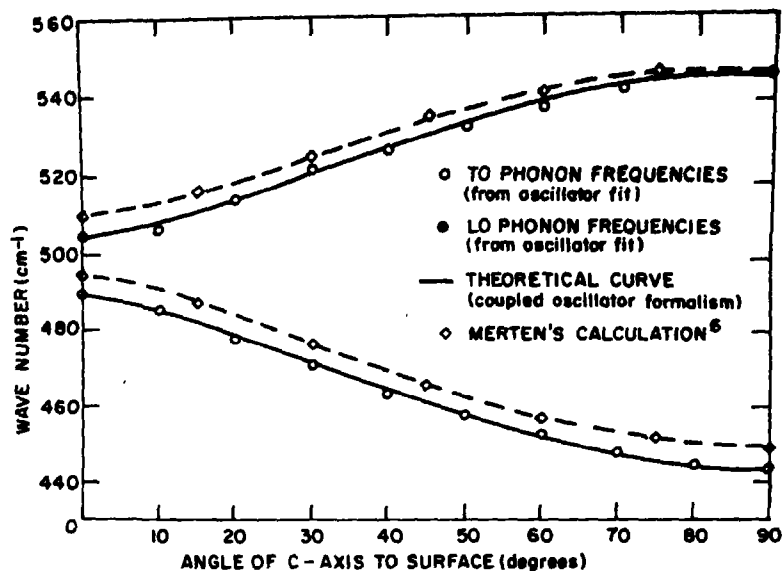


Fig. 8. Comparison of the calculated and measured frequencies of the $A_2(t) - E(t)$ mode and the $E(1) - A_2(1)$ mode as a function of the angle between the surface and the c -axis.

angle between the c -axis and the crystal surface. Analysis of the reflectivity data by K - K and harmonic oscillator formalisms has enabled us to extract the frequencies of the coupled phonon modes. The results of our experiments are in excellent agreement with calculations of the directional dispersion based on a coupled harmonic oscillator formalism.

The observation that a dip in the $E||c$ -axis reststrahlen peak near 500 cm^{-1} , as observed by Spitzer and Kleinman[3], results from mode coupling opens up other questions regarding the observation by other workers of forbidden modes in other uniaxial crystals. As in the case of MgF_2 and ZnF_2 [16], forbidden modes are observed most frequently in the $E||c$ geometry and occur very close to the LO phonon frequencies of modes for the other principal polarization. We suggest that in some cases one cannot dismiss a slight misalignment of the crystal or surface damage, and the resultant directional dispersion as being the source of the additional structure. There are probably

other cases where the occurrence of forbidden modes has a different origin, e.g. those observed in the $E \perp c$ -axis spectrum of $\alpha\text{-Al}_2\text{O}_3$ [17] may be due to relaxation of symmetry restrictions at an otherwise perfect crystal surface.

Acknowledgements—The authors wish to acknowledge helpful discussions with Professor E. Burstein of the University of Pennsylvania and R. Zallen of Xerox Corporation and the assistance of M. Slade of the Xerox Corporation in the programming of the dispersion analysis. Finally we wish to thank Mark Lucovsky for the use of a natural quartz crystal, on which preliminary measurements of this effect were made by one of the authors (G. L.).

REFERENCES

1. RUBENS H. and NICHOLS E. F., *Wiedemanns Ann. Phys.* **60**, 418 (1897).
2. BARNES R. B., *Phys. Rev.* **39**, 562 (1932).
3. SPITZER W. G. and KLEINMAN D. A., *Phys. Rev.* **121**, 1324 (1961).
4. SCOTT J. F. and PORTO S. P. S., *Phys. Rev.* **161**, 903 (1967).
5. LOUDON R., *Adv. Phys.* **13**, 423 (1964).
6. MERTEN L., *Phys. Status Solidi* **28**, 111 (1968).
7. LUCOVSKY G., BURSTEIN E. and PINCZUK A., *Bull. Am. phys. Soc.* **14**, 740 (1969).

8. MATHIEU J. P. and COUTRE-MATHIEU L., *C. r. hebd. Séanc. Acad. Sci. Paris* **234**, 161 (1952).
9. COUTRE-MATHIEU L., KETELAAR J. A. A., VEDDER W. and FAHRENFORT J., *J. chem. Phys.* **20**, 1492 (1952).
10. LOUDON R., *Light Scattering Spectra of Solids*. Springer, Berlin. (1969).
11. SCOTT J. F., paper presented at *Pacific Conf. on Chemistry and Spectroscopy*, San Francisco (1968).
12. ONSTOTT J. and LUCOVSKY G., *Bull. Am. phys. Soc.* **14**, 740 (1969); unpublished.
13. PINCZUK A., Ph.D. Thesis, University of Pennsylvania, Philadelphia (1969).
14. PAIHK E., HENVIS B. W., SAWADA Y. and BURSTEIN E., to be published.
15. MERTEN L., *Z. Naturf.* **22a**, 359 (1967).
16. BARKER A. S., Jr., *Phys. Rev.* **136**, A1290 (1964).
17. BARKER A. S., Jr., *Phys. Rev.* **132**, 1474 (1963).

STRUCTURES AND MAGNETIC PROPERTIES OF THE PSEUDO-BINARY SYSTEMS $\text{CeNi}_2\text{-CeCu}_2$ AND $\text{GdNi}_2\text{-GdCu}_2^*$

W. E. WALLACE, T. V. VOLKMANN and R. S. CRAIG
Department of Chemistry, University of Pittsburgh, Pittsburgh, Pa. 15213, U.S.A.

(Received 9 December 1969; in revised form 13 January 1970)

Abstract—The C15 (cubic Laves phase) structure exists over the range $x = 0$ to 0.35 in the ternary system $\text{GdNi}_{1-x}\text{Cu}_x$ and the orthorhombic GdCu_2 phase extends from $x = 1.1$ to 2.0. In contrast the solubility of CeCu_2 in CeNi_2 is below the limit of detectability. The magnetic behavior of the Gd-containing ternaries based on GdNi_2 closely resembles that of GdNi_2 . The susceptibility of CeNi_2 is very low compared to that expected for an assemblage of free Ce^{3+} ions. The ratio of expected to measured susceptibility is 3.5 at 300°K but rises to approximately 100 at 4.2°K. The susceptibility deficiency is too great to be ascribed solely to the effect of the crystal field although this may be a contributing factor. Partial ionization into Ce^{4+} and spin compensation (Kondo effect) by the conduction electrons may also be involved. Below 30°K $1/\chi$ varies as $T^{0.48}$ in keeping with the behavior expected if spin compensation were the dominant effect.

1. INTRODUCTION

A NUMBER of ternary systems containing the lanthanide elements (Ln) have recently been studied in this laboratory[1-6]. In the Laves phase systems $\text{LnCo}_2\text{-LnAl}_2$ and $\text{LnFe}_2\text{-LnAl}_2$ the results indicated[1] that the limit of the C15 terminal phase is reached at an electron concentration of about 1.16 electrons/atom. Similar results have been obtained more recently on the $\text{LnNi}_2\text{-LnAl}_2$ systems[7]. The phase boundary in these ternaries has been associated with the filling of the Brillouin Zone formed by the 220 planes. The present study was undertaken to ascertain whether similar behavior is exhibited when the electron concentration is increased by the use of Cu instead of Al as a replacement for Ni in the LnNi_2 Laves phase systems.

Work in the present study has been confined to two ternaries, $\text{Ln} = \text{Ce}$ and Gd . CeNi_2 and Ce-containing systems have recently become subjects of intense concern for a number of investigators for a variety of reasons. First, in regard to Ce-containing systems in

general they have been observed to exhibit the Kondo[8-10] phenomenon, and more importantly the behavior has been observed in systems in which the magnetic species giving rise to the Kondo effect is present in large concentration. Second, as regards CeNi_2 it has been found to possess a number of peculiarities when contrasted with other members of the LnNi_2 series. Its lattice parameter is anomalously low, which has been interpreted[11] to indicate a quadrivalent state for Ce in CeNi_2 . This conclusion was supported[12] by early susceptibility work on CeNi_2 which seemed to indicate it to be a Pauli paramagnet. More recently heat capacity studies[13] on CeNi_2 have revealed two anomalies: (1) a rising heat capacity for temperatures below 2.5°K, which resembles a hyperfine contribution but which cannot originate in this way since Ce lacks a nuclear magnetic moment and (2) a substantial excess heat capacity (of unexplained origin) over the Dulong-Petit limit at temperatures in excess of 200°K. Finally as regards the aberrant behavior of CeNi_2 it was found in the studies of $\text{LnNi}_2\text{-LnAl}_2$ systems referred to above[7]

*This work was assisted by the U.S. Atomic Energy Commission.

that CeNi_2 alone among the LnNi_2 compounds showed no solubility of LnAl_2 in the LnNi_2 -based phase.

The atypical behavior of CeNi_2 just described was responsible for choosing it as the principal substance of concern in the present study. The Gd ternaries were included as a 'normal' counterpart of the Ce-Ni-Cu ternaries. It was hoped that study of the former system would be useful in the interpretation of results obtained for the latter.

2. EXPERIMENTAL DETAILS

The techniques employed are standard in this laboratory. Samples were prepared by levitation melting using the purest metals obtainable commercially—99.99 per cent Ni and 99.9 per cent Ln, exclusive of gaseous impurities. The samples were all sealed off in evacuated Vycor tubes and annealed for three weeks. The Ce samples were annealed at 650°C, the Gd samples at 750°C. These temperatures were determined by experiment, the criterion being maximal improvement in the diffraction pattern. Structural information was obtained using a Ge XRD-5 diffractometer. Magnetic results were obtained by the Faraday method using equipment that has been described [14].

3. RESULTS AND DISCUSSION

CeNi_2 and GdNi_2 have the cubic Laves phase structure, C15. The lattice spacings observed were 7.197 and 7.207 Å, respectively, at room temperature. In view of the strange low temperature behavior of CeNi_2 its a parameter was also determined at 5°K; it was found to be 7.164 Å. CeCu_2 and GdCu_2 have the orthorhombic structures found by Storm and Benson [15]. The parameters (in Å) obtained are $a = 4.33$, $b = 6.87$ and $c = 7.34$ for GdCu_2 . CeCu_2 parameters were not established in this study.

The C15 phase extends from GdNi_2 to $\text{GdNi}_{1.65}\text{Cu}_{0.35}$; the unit cell size is the same over the range of stability of the C15 phase. The terminal phase based on GdCu_2 extends

to $\text{GdNi}_{2-x_c}\text{Cu}_{x_c}$ where $x_c = 1.10 \pm 0.15$. There is no detectable solubility of CeCu_2 in CeNi_2 . Ternaries with nominal Cu concentrations as low as $\text{CeNi}_{1.98}\text{Cu}_{0.02}$ were examined and found to consist of two phases. This finding is consistent with other related work which showed that CeAl_2 does not dissolve to any significant extent [7] in CeNi_2 .

The magnetic properties of the orthorhombic phase in the Gd-Ni-Cu ternaries were not determined. The C15 alloys in this system were examined. Results obtained were rather straightforward* and resembled closely the data obtained [12] for GdNi_2 . Comparison of results for GdNi_2 and the ternary at the phase boundary are given in Table 1.

The magnetic results obtained for CeNi_2 are largely summarized in Figs. 1–3. Results were obtained for a number of CeNi_2 samples. Data for only 4 samples are shown. Sample I

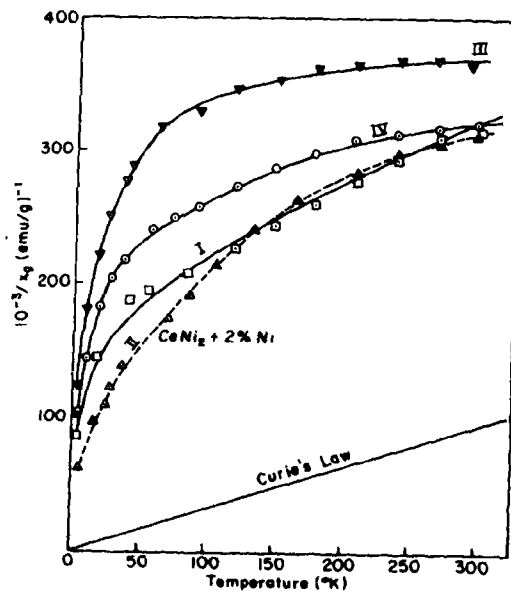


Fig. 1. Reciprocal susceptibility-temperature data (measured in an applied field of 20 kOe) for three CeNi_2 samples (I, III and IV) and one CeNi_2 sample deliberately contaminated with 2 wt. per cent excess Ni (II).

*The authors would like to express their appreciation to Dr. Burke Leon for assistance in connection with these measurements.

Table 1. Magnetic characteristics of GdNi_2 and $\text{GdNi}_{1.65}\text{Cu}_{0.35}$

	GdNi_2	$\text{GdNi}_{1.65}\text{Cu}_{0.35}$	
Ferromagnetic moment	7.1	6.80 ± 0.05	$gJ = 7.0$
Paramagnetic moment (μ_B per formula unit)	7.82	7.94 ± 0.05	$g\sqrt{J(J+1)} = 7.95$
Curie temperature ($^\circ\text{K}$)	85	103 ± 1	
Weiss constant ($^\circ\text{K}$)	78	92 ± 2	

* From data of Farrell and Wallace [12].

was prepared earlier in the study without undue care before the smallness of χ and the complexity of the nature of CeNi_2 was fully appreciated. Sample II was deliberately contaminated with nickel at the level of detectability in such systems [16]. The effect of the added nickel is clearly evident in the χ values in Fig. 1 and in the field dependence of the apparent χ (Figs. 2 and 3). Samples III and IV were the last of the preparations. They were prepared and annealed with exceptional care; their X-ray diffraction patterns were excellent both as regards line shape and doublet resolution. Despite the care with which III and IV were prepared significant deviations between their susceptibilities were observed. Data for sample III are regarded

as most nearly representative of the behavior of pure CeNi_2 .

The possibility must be considered that the samples are contaminated with one or more extraneous phase(s) and these give rise to the variable magnetic behavior. These phases must be present as rather minor components since the present and previous work [16] has shown that extra phases can be detected at the level of 2 per cent by diffraction techniques, which has proved to be the most sensitive method available for these systems. Hence if the variable χ is due to the presence of extraneous phases, they must have substantially different susceptibility behavior than CeNi_2 . The magnetic properties of CeNi [17] and CeNi_5 [18], the two

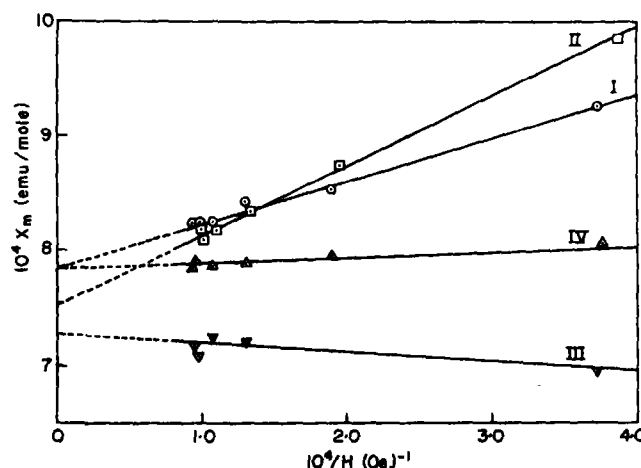


Fig. 2. Room temperature field dependency of the susceptibility of the CeNi_2 samples and a sample of CeNi_2 containing 2 wt. per cent excess nickel. The variation of χ with field for the two 'good' samples (III and IV) is almost within the limit of error of the measurement.

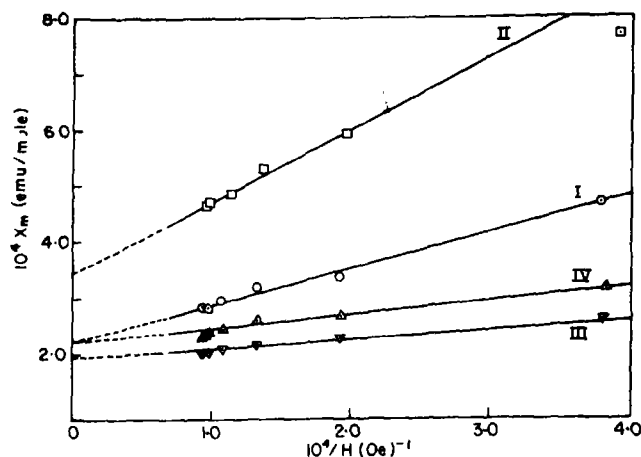


Fig. 3. Field dependency of the susceptibility at 4.2°K for the four samples of Figs. 1 and 2.

stable phases bracketing CeNi_2 , closely resemble those of CeNi_2 indicating only slight likelihood that the non-reproducible susceptibility is due to the presence of extra phases. Rather it seems to be due to traces of unreacted nickel, to nickel clusters at lattice imperfections or some such effect.

The most striking features of the CeNi_2 results are (a) the nonconformity with Curie-Weiss behavior and more significantly (b) the smallness of the susceptibility as compared with the values expected from Curie's law. The ratio of the ideal (i.e. Curie Law) susceptibility to that measured is 3.5 at 300°K and approximately 100 at 4.2°K. It is instructive to contrast the results shown in Fig. 1 with similar data for dilute CeAl_2 dissolved in LaAl_2 obtained by White *et al.*[19]. They found susceptibilities which approached the values computed from Curie's Law at higher temperatures; deviation between measured and calculated values were 10 per cent or less for $T > 200^\circ\text{K}$. For lower temperatures the susceptibility became lower than the ideal value, the deviation gradually increasing from about 10 per cent at 200°K to about 75 per cent at 10°K. The deviations were ascribed by White *et al.* to the influence of the crystal

field. The cubic field in these materials results in a partial lifting of the 6-fold degeneracy of tripositive cerium ion[20]. Either a Γ_7 (doublet) or Γ_8 (quartet) ground state is produced depending on the sign of the crystal field interaction. White *et al.* interpreted their result to indicate that the Γ_7 state was lowest lying; in this case χ is reduced by 5/21 as compared with the ideal value. If, however, the Γ_8 state is lowest this factor is 13/21 in the low temperature limit.

Since χ_{meas} is less than χ_{ideal} by a factor of 100, it is clear that the reduced susceptibility at low temperatures cannot be solely due to the crystal field interaction; this could at most reduce χ by a factor of 4.2 as compared to the ideal value. Formally the susceptibility deficiency could be accounted for by assuming that 96 per cent of the cerium ions are quadrivalent. It seems unlikely, however, that the situation is this simple. It appears that the heat capacity anomalies must be related to the population of magnetic ions and it seemed unlikely, but perhaps not impossible, that 4 per cent of the cerium ions could give rise to the observed heat capacity effects. There is yet another factor which argues against such a large content of quadrivalent cerium: studies

[1, 2, 21] of a large number of ternary Laves phases between the lanthanides and the d -transition metals make it quite clear that the C15 phase is unstable of electron concentrations (e.c.) in excess of about 1.16. CeNi_2 containing 96 per cent Ce^{+4} would have an e.c. of 1.32 and while this is not impossible, it does seem on the basis of earlier experience to be rather unlikely. Elsewhere from the study of $\text{CeNi}_{2-x}\text{Al}_x$ ternaries [7] it has been concluded that the fraction of Ce which is quadrivalent in CeNi_2 is ≥ 0.3 . The anomalously low lattice parameter [11] of CeNi_2 suggests that a portion of Ce is in the +4 state but the extent of ionization of Ce^{+3} cannot be estimated from this source alone. These observations do provide suggestive evidence indicating the f level to lie close to or probably slightly above the Fermi energy. Detailed information about the band structure in CeNi_2 is lacking; it is sorely needed for a full interpretation of the behavior of CeNi_2 .

The reduced susceptibility of CeNi_2 is probably due to spin-compensation of the Ce^{+3} moment (Kondo effect) or possibly this in conjunction with the reduction by the crystal field alluded to above. Anderson [22] has indicated that if spin compensation is the dominant effect in determining the low temperature magnetic behavior of an assemblage of magnetic ions, χ varies as $T^{-1/2}$ in the low temperature limit. The data plotted [23] in Fig. 4 indicate that $1/\chi$ is linear with T^a where

a is very close to 0.5 (actually 0.48) for $T < 20^\circ\text{K}$. This supports the notion that spin compensation is occurring in CeNi_2 although conductivity measurements on CeNi_2 have so far failed to reveal the expected minimum in resistance [24]. There are two possible reasons why experiments to date have failed to reveal a resistance minimum: (1) it may occur at a temperature in excess of 300°K , above the range of temperature covered in studies to date; (Nakamura *et al.* [25] have observed Kondo minima in magnetically concentrated systems in the temperature range 500 – 700°K); (2) the minima may be obscured by other effects which influence the conductivity—the crystal field effect and/or the change in valence. Each of these significantly affects the spin disorder scattering contribution to the resistance and, moreover, they are temperature dependent. The lack of a resistance minimum is not altogether unexpected if the Kondo temperature is high, for then the phonon scattering is large and the influence of spin compensation is minor and easily obscured by the other effects.

REFERENCES

1. OESTERREICHER H. and WALLACE W. E., *J. less-common Metals* **13**, 91 and 475 (1967).
2. MAREI S., CRAIG R. S., WALLACE W. E. and TSUCHIDA T., *J. less-common Metals* **13**, 391 (1967).
3. WALLACE W. E., HOPKINS H. P., Jr. and LEHMAN K., *J. Solid-St. Chem.* **1**, 39 (1969).
4. MADER K. H. and WALLACE W. E., *J. chem. Phys.* **49**, 1521 (1968).

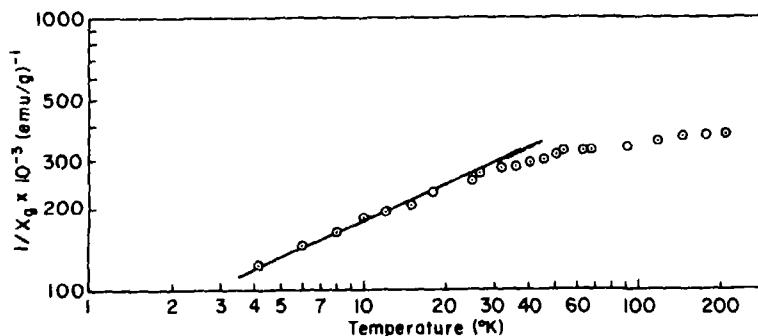


Fig. 4. Log-log plot of $1/\chi_g$ vs. temperature for CeNi_2 . At low temperatures the plot approaches linearity with a slope of 0.48.

5. SWIFT W. M. and WALLACE W. E., *J. Phys. Chem. Solids* **29**, 2053 (1968).
6. MADER K. H., SEGAL E. and WALLACE W. E., *J. Phys. Chem. Solids* **30**, 1 (1969).
7. LEON B. and WALLACE W. E., *J. less-common Metals* (In press).
8. SUGAWARA T. and YOSHIDA S., *J. phys. Soc. Japan* **24**, 1399 (1968).
9. HILL H. H., ELLIOTT R. O. and MINOR V. N., *7th Rare Earth Conf. Proc., Coronado, Calif.* (1968).
10. VAN DAAL H. J. and BUSCHOW K. H. J., *7th Rare Earth Conf. Proc., Coronado, Calif.* (1968).
11. WALLACE W. E., *Progress in Rare Earth Science and Technology* (Edited by L. Eyring), Vol. 3, p. 1. Pergamon Press, Oxford (1968).
12. FARRELL J. and WALLACE W. E., *Inorg. Chem.* **5**, 105 (1966).
13. WALLACE W. E., CRAIG R. S., THOMPSON A., DEENADAS C., DIXON M., AOYAGI M. and MARZOUK N., *CNRS Colloquium on Rare Earths*, To appear.
14. BUTERA R. A., CRAIG R. S. and CHERRY L. V., *Rev. scient. Instrum.* **32**, 708 (1961).
15. STORM A. R. and BENSON K. E., *Acta crystallogr.* **16**, 701 (1963).
16. CARFAGNA P. D. and WALLACE W. E., *J. appl. Phys.* **39**, 5259 (1968).
17. WALLINE R. E. and WALLACE W. E., *J. chem. Phys.* **41**, 1587 (1964).
18. AOYAGI M. and WALLACE W. E., Unpublished measurements from this laboratory.
19. WHITE J. A., WILLIAMS H. J., WERNICK J. H. and SHERWOOD R. C., *Phys. Rev.* **131**, 1039 (1963).
20. LEA K. R., LEASK M. J. M. and WOLF W. P., *J. Phys. Chem. Solids* **23**, 1381 (1962).
21. SHIDLOVSKY I. and WALLACE W. E., *J. Solid St. Chem.* In press.
22. ANDERSON P. W., *Phys. Rev.* **164**, 352 (1967).
23. The authors are grateful to Dr. V. U. S. RAO for drawing attention to this feature of the magnetic results obtained for CeNi₂.
24. CRAIG R. S. and RAO V. U. S., Unpublished data from this laboratory.
25. NAKAMURA Y., INOUE Y., KUNITOMI N. and NAKAI Y., *J. phy. Soc. Japan*, **24**, 1398 (1968).

A DIELECTRIC CALCULATION OF ENERGY LOSS TO VALENCE ELECTRONS UNDER CHANNELING CONDITIONS*

F. BONSIGNORI† and A. DESALVO

Istituto di Fisica, Università di Bologna, Istituto Nazionale di Fisica Nucleare, Sezione di Bologna, Gruppo Nazionale di Struttura della Materia del C.N.R. Italy

(Received 14 October 1969; in revised form 12 January 1970)

Abstract—The decrease in the contribution of valence electrons to the stopping power under channeling conditions has been evaluated by taking into account the Fourier components with $G \neq 0$ of the response function: explicit calculations were carried out in the weak-binding limit. The particular case of 100 keV protons travelling at the center of [001] channel in gold has been calculated in detail. The decrease in the valence electron contribution to the stopping power in channeling, turns out to be much smaller than the decrease of local electron density at midchannel axis. These results are in reasonable agreement with the experimental ones obtained in this laboratory.

1. INTRODUCTION

THE AIM of this paper is to calculate how much the valence electrons contribution to the stopping power of a fast charged particle decreases under channeling conditions.

The first treatment of the problem, due to Lindhard[1], relies upon the partition between close and distant collisions. In the limit of high incident particle velocity, even though not relativistic, both contribute equally to the energy loss for an unchanneled beam (equipartition rule). In this model close collisions are assumed to be proportional to the local electron density and distant collisions to the average one. Under channeling conditions the incident particle experiences a local electron density less than the average, the contribution of the close collisions to the stopping power being reduced accordingly. As a consequence the largest reduction of the stopping power amounts to a factor of two, which happens when the local electron density becomes negligible. While the first experimental results were in agreement with this model, further

experiments[2] showed that the agreement was partly fortuitous and the relative decrease of the stopping power is more frequently less than 50 per cent and is dependent upon the particle energy and the target element.

Erginsoy worked out a different model analyzing separately the contribution of core and valence electrons to the stopping power [3, 4]. The former are treated semiclassically expressing the usual Bethe-Bloch formula in terms of impact parameters. When the maximum impact parameter for a certain shell $b_{\max}$, is less than the minimum distance of approach of a channeled particle to an atom b_{ch} , the contribution of such a shell to the energy loss turns out to be zero. Otherwise such a contribution scales by a factor depending on $\ln(b_{\max}/b_{ch})$ ‡.

As for the valence electrons, Erginsoy regards their contribution quite insensitive to the channeling conditions and describes them as a free electron gas. The energy loss to valence electrons is still separated, as in Lindhard's model, in a contribution due to close

*Work carried out under the U.S.-Italy Cooperative Program in Science (CNR grant 69.00027).

†Now at Strasbourg, Laboratoire de Physique des Solides, Institut de Physique.

‡ $b_{\max}$ is determined by the so-called adiabatic condition $b_{\max} = \hbar v / \Delta E$, where v is the particle velocity and ΔE the excitation energy of the shell; b_{ch} for wellchanneled particles can be as high as the half-width of the channel [3, 4].

collisions, proportional to the local electron density, and in a contribution due to distant collisions, proportional to the average one. The two terms correspond to collisions with momentum transfer greater and lower than $k_F = \omega_p/v_F$ respectively, and this takes into account automatically departures from equipartition. The local valence electron density determined in this case turns out to be very close to the average one [4].

A completely different model, based on the excitation of collective modes (distant collisions) under channeling conditions, has been developed by Brice [5]. He does not make a separation between core and valence electrons, but simply introduces an effective number of electrons participating to the collective excitation. This number is taken as a parameter to be determined from the experimental results; the latter show that it is lower the more open the channel is.

Comparing with the experiments both Erginsoy and Brice's theory it is apparent that a large part of the stopping power decrease in channeling is due to a smaller excitation probability of inner shell electrons. All these theories leave still open the problem of the decrease in the valence electron contribution to the stopping power in channeling.

Furthermore the analysis of such a decrease is of particular interest in order to use channeling experiments to get informations on electron density [4, 6, 7].

We have treated the problem in terms of dielectric constant, without making recourse to the simplifications used by Lindhard [1] and Erginsoy [3]. An outline of our method has been already published elsewhere [8]. Essentially we take into account that the electron gas is not spatially uniform but has the lattice periodicity.

Under channeling conditions the incident particle explores only a certain region of the cell: therefore the local effects due to the Fourier components with $\mathbf{G}$ different from zero of the response function [9] will also be important. As is well known the imaginary

part of this function determines the energy loss.

Our first main approximation is to limit ourselves to the weak-binding case. Under this assumption the explicit expression for the response function, neglecting exchange, has been calculated by Falk [10] and is given by:

$$\mathcal{K}(\mathbf{q}, \mathbf{G}, \omega) = \delta_{\mathbf{G},0} \frac{1}{1 + \alpha(\mathbf{q}, 0, \omega)} - (1 - \delta_{\mathbf{G},0}) \frac{\alpha(\mathbf{q}, \mathbf{G}, \omega)}{1 + \alpha(\mathbf{q}, 0, \omega)} \quad (1)$$

where

$$\alpha(\mathbf{q}, \mathbf{G}, \omega) = -\frac{4\pi e^2}{\Omega |\mathbf{q} + \mathbf{G}|^2} \sum_{j,\beta} \langle \beta | \exp[i\mathbf{q} \cdot \mathbf{r}] | j \rangle \times \langle j | \exp[-i(\mathbf{q} + \mathbf{G}) \cdot \mathbf{r}] | \beta \rangle \quad (2)$$

$$\times \left[\frac{1}{\hbar\omega - (E_\beta - E_j) + i\eta} - \frac{1}{\hbar\omega + (E_\beta - E_j) + i\eta} \right]$$

(Ω = volume; j, β initial and final states; here and in the following, the limit $\eta \rightarrow 0$ is to be understood.)

We notice that the real and imaginary part of α can be easily written down, when the matrix elements are real, as e.g. occurs in a centrosymmetrical lattice.

When $\epsilon_{0,1}$ and $\epsilon_{0,2}$ are different from zero, i.e. in the region of single particle excitation, the imaginary part of the 'local' response function, is given by [8]

$$\begin{aligned} \text{Im } \mathcal{K}(\mathbf{q}, \omega, \mathbf{r}) &= \text{Im} \sum_{\mathbf{G}} \mathcal{K}(\mathbf{q}, \mathbf{G}, \omega) e^{i\mathbf{G} \cdot \mathbf{r}} \\ &= \text{Im} \frac{1 - \sum_{\mathbf{G} \neq 0} \alpha(\mathbf{q}, \mathbf{G}, \omega) e^{i\mathbf{G} \cdot \mathbf{r}}}{1 + \alpha(\mathbf{q}, 0, \omega)} \\ &= -\frac{\epsilon_{0,2}}{\epsilon_{0,1}^2 + \epsilon_{0,2}^2} \left\{ 1 + \sum_{\mathbf{G} \neq 0} \left[\left(\frac{\epsilon_{0,1}}{\epsilon_{0,2}} \epsilon_{\mathbf{G},2} - \epsilon_{\mathbf{G},1} \right) \right. \right. \\ &\quad \times \cos \mathbf{G} \cdot \mathbf{r} + \left. \left(\frac{\epsilon_{0,1}}{\epsilon_{0,2}} \epsilon_{\mathbf{G},1} + \epsilon_{\mathbf{G},2} \right) \sin \mathbf{G} \cdot \mathbf{r} \right] \right\} \quad (3) \end{aligned}$$

where

$$\epsilon_{G,1} + i\epsilon_{G,2} = \epsilon(\mathbf{q}, \mathbf{G}, \omega) = \delta_{G,0} + \alpha(\mathbf{q}, \mathbf{G}, \omega). \quad (4)$$

On the contrary, when $\epsilon_{0,1} = \epsilon_{0,2} = 0$, i.e. along the undamped plasmon line*, we obtain, proceeding as for the uniform electron gas [11]:

$$\begin{aligned} \text{Im } \mathcal{K}(\mathbf{q}, \omega, \mathbf{r}) &= \text{Im} \sum_{\mathbf{G}} \mathcal{K}(\mathbf{q}, \mathbf{G}, \omega) e^{i\mathbf{G} \cdot \mathbf{r}} \\ &= \text{Im} \frac{1 - \sum_{\mathbf{G} \neq 0} \alpha(\mathbf{q}, \mathbf{G}, \omega) e^{i\mathbf{G} \cdot \mathbf{r}}}{1 + \alpha(\mathbf{q}, 0, \omega)} \\ &= \text{Im} \lim_{\epsilon_{0,1}} \frac{1 - \sum_{\mathbf{G} \neq 0} \epsilon_{G,1} e^{i\mathbf{G} \cdot \mathbf{r}}}{\epsilon_{0,1}} \\ &= -\frac{\pi \left(1 - \sum_{\mathbf{G} \neq 0} \epsilon_{G,1} \cos \mathbf{G} \cdot \mathbf{r} \right)}{(\partial \epsilon_{0,1} / \partial \omega)_{\omega=\omega_p}} \delta(\omega - \omega_p). \quad (5) \end{aligned}$$

By averaging over a region large compared with the unit cell all the terms but $-(\epsilon_{0,2}/\epsilon_{0,1}^2 + \epsilon_{0,2}^2)$ in (3) and $-\pi\delta(\omega - \omega_p)/(\partial \epsilon_{0,1}/\partial \omega)_{\omega=\omega_p}$ in (5) cancel out; these terms are just the ones employed to calculate the stopping power in a uniform electron gas or when the crystal structure is not important.

2. DESCRIPTION OF THE MODEL

As already mentioned we restricted for simplicity to the nearly free electrons case and introduce essentially a two-band model. However in order to take into account the crystal orientation, the simple spherical Penn's model [12] is not sufficient. On the other hand a detailed treatment of the Brillouin zones makes the calculations unmanageable. Therefore we built an intermediate model, which makes the calculations tractable but at the same time includes the essential features to calculate energy loss under channeling conditions, i.e. non uniform space distribution of the electron gas and enough lattice symmetry to single out crystallographic directions.

*Outside the single particle excitation spectrum, not only $\epsilon_{0,2} = 0$, but also $\epsilon_{G,2} = 0$ (at least as long as the matrix elements are real).

We consider an f.c.c. lattice, because the experiments in this laboratory are carried out on gold [13]. The first Brillouin zone has been approximated by a sphere divided in 14 equivalent sectors, one for each first and second neighbour of the reciprocal lattice. The sphere radius, in the following denoted k_D , was obtained as usually for the Debye sphere. The second Brillouin zone was obtained by translating each sector of the first zone by a vector $-2k_D \hat{\mathbf{k}}$, where $\hat{\mathbf{k}}$ is a unit vector in the direction of the reciprocal lattice vector which lies in the sector.

In each sector the wave function was approximated as follows

$$\Psi_{\mathbf{k}} = \frac{1}{\sqrt{\Omega}} \frac{e^{i\mathbf{k} \cdot \mathbf{r}} + C_{\mathbf{k}} e^{i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}}}{\sqrt{1 + C_{\mathbf{k}}^2}} \quad (6)$$

where

$$\begin{aligned} C_{\mathbf{k}} &= -\frac{1}{2} \frac{E_g}{E_{\mathbf{k}} - E_{\mathbf{k}+\mathbf{G}}^0} \\ E_{\mathbf{k}}^0 &= \frac{\hbar^2}{2m} k^2 \\ E_{\mathbf{k}} &= \frac{1}{2} \{ E_{\mathbf{k}}^0 + E_{\mathbf{k}+\mathbf{G}}^0 \pm \sqrt{(E_{\mathbf{k}}^0 - E_{\mathbf{k}+\mathbf{G}}^0)^2 + E_g^2} \} \end{aligned} \quad (7)$$

(E_g energy gap, $\mathbf{G} = -2k_D \hat{\mathbf{k}}$ and the minus sign is for the lower and plus for the upper band respectively).

The energy gap was taken 6 eV, on the ground of the values determined for copper [14]. With this value the decrease of electron density at midchannel axis, averaged along the [001] axis, turns out to be 16 per cent of the mean density.

We point out that the possibility of comparison of the results obtained by this model with experiments is limited by having neglected *d*-electrons. The evaluation of this contribution requires a more elaborate treatment and further investigations in this direction are envisaged.

We notice that in our case, since we are dealing with a metal, the lower band is only half full, contrary to the more usually con-

sidered intrinsic semiconductor [12, 15]. The perturbation of the free electron values remains reasonably small up to $k = k_F$ ($C_{k_F} = 0.38$, so it is reasonable to consider $C_k^2 \ll 1$).

The eigen-functions (6) must be introduced in (2) to calculate the matrix elements. The summation which appears there, can be divided as usual in terms corresponding to $G = 0$ and $G \neq 0$ so giving rise to a 'Normal' and an 'Umklapp' term.

We obtain

$$\begin{aligned} \alpha(\mathbf{q}, 0, \omega) = & -\frac{4\pi e^2}{\Omega q^2} \left\{ \sum_{\mathbf{k}, \mathbf{k}+\mathbf{q}} n_{\mathbf{k}}(1-n_{\mathbf{k}+\mathbf{q}}) \right. \\ & \times \frac{(1+C_k C_{\mathbf{k}+\mathbf{q}} \delta_{\mathbf{k}, \mathbf{k}+\mathbf{q}})^2}{(1+C_k^2)(1+C_{\mathbf{k}+\mathbf{q}}^2)} \left[\frac{1}{\hbar\omega - (E_{\mathbf{k}+\mathbf{q}} - E_{\mathbf{k}}) + i\eta} \right. \\ & \left. \left. - \frac{1}{\hbar\omega + (E_{\mathbf{k}+\mathbf{q}} - E_{\mathbf{k}}) + i\eta} \right] + \sum_{\mathbf{k}, \mathbf{k}+\mathbf{q}+\mathbf{G}} n_{\mathbf{k}}(1-n_{\mathbf{k}+\mathbf{q}+\mathbf{G}}) \right. \\ & \times \frac{(C_k \delta_{\mathbf{k}, \mathbf{k}+\mathbf{q}} + C_{\mathbf{k}+\mathbf{q}+\mathbf{G}})^2}{(1+C_k^2)(1+C_{\mathbf{k}+\mathbf{q}+\mathbf{G}}^2)} \\ & \times \left[\frac{1}{\hbar\omega - (E_{\mathbf{k}+\mathbf{q}+\mathbf{G}} - E_{\mathbf{k}}) + i\eta} \right. \\ & \left. \left. - \frac{1}{\hbar\omega + (E_{\mathbf{k}+\mathbf{q}+\mathbf{G}} - E_{\mathbf{k}}) + i\eta} \right] \right\} \end{aligned} \quad (8)$$

where $\delta_{\mathbf{k}, \mathbf{k}+\mathbf{q}}$ means that $\mathbf{k}$ and $\mathbf{k}+\mathbf{q}$ lie in the same sector, instead of the usual definition $\mathbf{k} = \mathbf{k}+\mathbf{q}$. We notice that these terms are important only in the limit $\mathbf{q} \rightarrow 0$: we kept them explicitly in order to obtain the exact shape of the plasmon excitation spectrum. For the calculation of C_k , we use the simpler Penn's model, i.e. we put $\mathbf{G}$ parallel to $\mathbf{k}$.

In the same way one obtains, taking only the linear terms in C_k ,

$$\begin{aligned} \alpha(\mathbf{q}, \mathbf{G}, \omega) = & -\frac{4\pi e^2}{\Omega |\mathbf{q}+\mathbf{G}|^2} \left\{ \sum_{\mathbf{k}, \mathbf{k}+\mathbf{q}} n_{\mathbf{k}}(1-n_{\mathbf{k}+\mathbf{q}}) \right. \\ & \times \frac{C_k \delta_{\mathbf{k}, \mathbf{G}} + C_{\mathbf{k}+\mathbf{q}} \delta_{\mathbf{k}+\mathbf{q}, -\mathbf{G}}}{(1+C_k^2)(1+C_{\mathbf{k}+\mathbf{q}}^2)} \times \left[\frac{1}{\hbar\omega - (E_{\mathbf{k}+\mathbf{q}} - E_{\mathbf{k}}) + i\eta} \right. \end{aligned}$$

$$\begin{aligned} & \left. - \frac{1}{\hbar\omega + (E_{\mathbf{k}+\mathbf{q}} - E_{\mathbf{k}}) + i\eta} \right] + \sum_{\mathbf{k}, \mathbf{k}+\mathbf{q}+\mathbf{G}} n_{\mathbf{k}}(1-n_{\mathbf{k}+\mathbf{q}+\mathbf{G}}) \\ & \times \frac{C_k \delta_{\mathbf{k}, \mathbf{k}+\mathbf{q}} + C_{\mathbf{k}+\mathbf{q}+\mathbf{G}} \delta_{\mathbf{k}+\mathbf{q}, -\mathbf{G}}}{(1+C_k^2)(1+C_{\mathbf{k}+\mathbf{q}+\mathbf{G}}^2)} \\ & \times \left[\frac{1}{\hbar\omega - (E_{\mathbf{k}+\mathbf{q}+\mathbf{G}} - E_{\mathbf{k}}) + i\eta} \right. \\ & \left. \left. - \frac{1}{\hbar\omega + (E_{\mathbf{k}+\mathbf{q}+\mathbf{G}} - E_{\mathbf{k}}) + i\eta} \right] \right\} \end{aligned} \quad (9)$$

where $\delta_{\mathbf{k}, \mathbf{G}}$ restricts the summation to values of $\mathbf{k}$ lying in the 'sector' $\mathbf{G}$.

We point out that further terms in (9) are of third order in C_k and therefore were dropped out. Moreover in the explicit evaluation, also the term $C_k \delta_{\mathbf{k}, \mathbf{k}+\mathbf{q}}$ was neglected, since it is important only to remove the divergence in the limit $\mathbf{q} \rightarrow 0$, which does not appear here. In principle, as it appears only when $\mathbf{k}$ and $\mathbf{k}+\mathbf{q}$ lie simultaneously in the 'sector' $\mathbf{G}$, it turns out to be smaller of a factor 14 than the term $C_{\mathbf{k}+\mathbf{q}+\mathbf{G}}$.

The 'local' stopping power is given by [8]:

$$\begin{aligned} -\frac{dE}{dx}(\mathbf{r}) = & \text{const} \int \frac{d^3\mathbf{q}}{q^2} \omega d\omega \\ & \times \text{Im} \mathcal{H}(\mathbf{q}, \omega, \mathbf{r}) \delta(\omega - \mathbf{q} \cdot \mathbf{v}) \end{aligned} \quad (10)$$

where $\mathbf{v}$ is the particle velocity.

By integrating along all the particle path all the terms but those for which $\mathbf{G}$ is normal to the channel axis (see equations (3) and (5)) cancel out. In fact just these terms do not contain a component of $\mathbf{r}$ parallel to the channel axis and therefore do not disappear by integrating over a lattice distance along the direction of propagation of the incident particle.

The energy loss was calculated for [001] axial channeling, with the particle path at mid-channel axis. Taking into account that $G_{200} = 2\pi/a$ ($2, 0, 0$) and $r = (a/4, a/4, z)$, where a is the lattice constant*, one obtains for single

*In this case the exact value of G , instead of the average value $2k_D$ used for the eigenfunction, has been employed, since here we compare with the exact value of particle position.

particle excitation (see equation (3)):

$$\text{Im } \mathcal{K}(\mathbf{q}, \omega, \mathbf{r}) = -\frac{\epsilon_{0,2}}{\epsilon_{0,1}^2 + \epsilon_{0,2}^2} \times \left\{ 1 - \sum_{\mathbf{G} \neq 0}' \left[\left(\frac{\epsilon_{0,1}}{\epsilon_{0,2}} \epsilon_{\mathbf{G},2} - \epsilon_{\mathbf{G},1} \right) \right] \right\} \quad (11)$$

where Σ' is limited to the $\mathbf{G}$'s normal to [001] axis.

We consider now the contribution of plasmon excitation to the stopping power. In the usual case of a free electron gas, the condition for plasmon existence is given by:

$$\epsilon_{0,1} = \epsilon_{0,2} = 0. \quad (12)$$

We notice that also in our weak-binding case the undamped plasmon dispersion relation is still simply given by (12). This arises from the form of the response function (1), whose denominator contains only $\epsilon_{0,1} + i\epsilon_{0,2}$ as for free electrons.

However, in the more complex case of a crystal, plasmons can be damped due to interband transitions[11]. For simplicity we made the assumption of small damping, i.e. $\epsilon_{0,2} \ll 1$, even though in our case this condition is not completely fulfilled: therefore our

evaluation can be considered as an upper limit for plasmon contribution.

Under these assumptions the dispersion relation of the real part of plasma frequency, for the Fourier component with $\mathbf{G} = 0$ of the response function, is given by $\epsilon_{0,1} = 0$ [16].

This condition remains valid in our case of weak-binding also for the other Fourier components of the response function, for the same reasons mentioned above for the no-damping case.

Computer calculations show that plasmon excitation spectrum is strongly modified compared to the free electron case (Fig. 1). The plasma line is split in two branches.*

Two main reasons justify this fact: the first is the appreciable value of the energy gap; the second is the fact that the lower band is only half full and Normal and Umklapp transitions, both intra and interband, must be taken into account, giving rise to a complicated $\mathbf{q}$ dependence. A more detailed account on this subject is planned.

*We notice that the appearance of these two branches is different from that found by other authors[17]. We point out also that only the upper branch is damped by Umklapp processes.

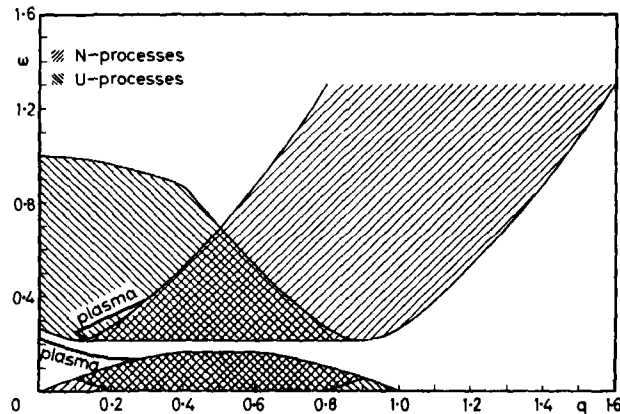


Fig. 1. Excitation spectrum for our model. Contribution from Normal and Umklapp processes are shown with different hatching. The two branches of the plasma line, along which $\epsilon_{0,1} = 0$, are also shown. ω and q are in the non-dimensional units quoted in the text.

Under the assumption of small damping and $\epsilon_{0,2}$ (and a fortiori $\epsilon_{G,2}$) $\ll 1$ we can use equation (5); under our channeling conditions we obtain:

$$\text{Im } \mathcal{K}(\mathbf{q}, \omega, \mathbf{r}) = -\frac{\pi \left(1 + \sum'_{\mathbf{G} \neq 0} \epsilon_{\mathbf{G},1}\right)}{(\partial \epsilon_{0,1} / \partial \omega)_{\omega=\omega_p}} \delta(\omega - \omega_p). \quad (13)$$

3. NUMERICAL CALCULATION AND DISCUSSION

Throughout our calculations we used non-dimensional units homogeneous with the model, i.e. $2k_D$ as unit for wavevectors and $4(\hbar^2 k_D^2 / 2m) = 4E_D$ for energy.

The electronic and lattice parameters were fixed as follows

$$k_D = \frac{2\pi}{a} \sqrt{\frac{3}{\pi}} = 1.52 \text{ \AA}^{-1} \quad (\text{gold})$$

$$\frac{k_F}{2k_D} = \frac{1}{2\sqrt{2}} = 0.4 \quad (\text{half full band})$$

$$E_0/4E_D = 0.17.$$

The energy of the incident particles was assumed to be 100 keV as in the experiments carried out in this laboratory [13]*. A suitable non-dimensional parameter for this type of calculations is $mv/\hbar k_D = v/v_D$ which turns out to be $v/v_D = 2.51$.

In the numerical computation of the contribution to stopping power due to close collisions, points lying on the upper plasmon branch were not taken into account: more precisely, a band of width $\Delta\omega = \pm 0.05$ around the plasma line, which is more realistic because of damping, was not taken into account.

In the numerical computation of plasmon contribution to the energy loss, the small region with a negative slope of the upper branch (see Fig. 1, around $\mathbf{q} \sim 0.1$) was neglected: in fact the calculations show that $\epsilon_{0,1}$ varies very strongly in this region; therefore, while the exact value of $|\partial \epsilon_{0,1} / \partial \omega|^{-1}$ (see

equation (13)) is very small, the error made in its numerical evaluation can be very large.

Table 1 shows the results of the numerical computation. The first column gives the contribution from close collisions to the stopping power in a random orientation, i.e. the term originating from $-(\epsilon_{0,2}/\epsilon_{0,1}^2 + \epsilon_{0,2}^2)$ in (11).

Table 1.

Calculated contributions to stopping power in 10^2 MeV/cm			
Single particle excitation		Plasmon excitation	
Random stopping power	Channeling effect	Random stopping power	Channeling effect
3.18	-0.04	1.36	-0.02

The major contribution to the stopping power arises, as usual, from the region around $\mathbf{q} \approx k_c$, $\omega = \omega_p(k_c)$ ($k_c \approx 0.3$ and $\omega_p(k_c) \approx 0.4$ in our case, see Fig. 1) [15, 18].

The calculations show also that the contribution from the region of Fig. 1, in which only Umklapp processes occur, is 0.84×10^2 meV/cm, i.e. about $\frac{1}{4}$ of the total value.

The second column is the correction to this term, i.e. it stems from the term

$$-\frac{1}{\epsilon_{0,1}^2 + \epsilon_{0,2}^2} \sum'_{\mathbf{G} \neq 0} (\epsilon_{\mathbf{G},1} \epsilon_{0,2} - \epsilon_{\mathbf{G},2} \epsilon_{0,1})$$

in (11), and gives the variation of close collision contribution to the stopping power due to channeling.

The third column gives the contribution from distant collisions (plasmon excitation) to the stopping power in a random orientation, while the fourth one gives the effect of channeling upon it, i.e. it corresponds to the term

$$-\pi \sum'_{\mathbf{G} \neq 0} \epsilon_{\mathbf{G},1} / \left(\frac{\partial \epsilon_{0,1}}{\partial \omega} \right)_{\omega=\omega_p}$$

in (13).

*In this energy range only valence electrons (6s and 5d) contribute appreciably to the energy loss.

The first important fact shown by this table is that there is no equipartition between close and distant collisions. In fact the ratio $-(dE/dx)_{\text{dist}}/-(dE/dx)_{\text{close}}$ is equal to 0.4. This value can be compared with the ones computed by Erginsoy[3], by interpolating his results according to our values of the various parameters: one obtains in this case a value of ~ 0.5 . We must remark, however, that Erginsoy's computations are made for a free electron gas ($E_F = 0$). Our result is thus in agreement with Brandt and Reinheimer's conclusion that in an electron gas close collisions contribute more and more than plasmons excitation to the stopping power with increasing energy gap [19].

The effect of channeling on single particle excitation probability turns out to be very small ~ 1.25 per cent, i.e. much smaller than the variation in the electron density, which is 16 per cent less than the average at midchannel axis in our model.

The detailed analysis of the partial computations shows that two factors can contribute to this strong reduction of the effect. First of all the decrease in electron density and in stopping power arise from different averages over the C_k 's. The former is a simple average over the Fermi sphere while the latter is weighted through the factor between square brackets in (9).

Secondly, as can be seen from (9), to the channeling term contribute both the C_k 's of the initial states, which lie in the lower band, and the C_{k+q} and C_{k+q+G} 's of the final states, which lie mostly in the upper band. The former and the latter have therefore opposite sign which tends to produce a certain amount of cancellation.

As a matter of fact, the detailed calculations show that the two contributions of opposite sign arise from different regions of the excitation spectrum of Fig. 1, roughly separated by the value $q \approx 0.8$. The probability for excitation with $q \gtrsim 0.8$ decreases under channeling conditions: with increasing q in fact C_{k+q} and C_{k+q+G} go to zero, giving a vanishing contri-

bution. This situation is in agreement with the usual classical interpretation in terms of small impact parameter collisions, sensitive to the local electron density. What is not expected on the basis of a classical theory is the opposite sign of the contribution from the other region, which roughly corresponds to inter-band excitations with $q < 0.8$. An intuitive picture of this fact may be given, taking into account the well known fact that lower band states are associated with a minimum electron density between atom rows and planes, while upper band states are associated with a maximum electron density at the same positions.

The result that the relative decrease in stopping power is much lower than the one in electron density, can also be understood on the basis of the semiclassical model of Erginsoy. Close collisions correspond to impact parameters varying from $b_{\text{min}} \approx \hbar/2mv$ to $b_c = k_c^{-1} = v_F/\omega_p$ [4]: therefore in this model the 'local' electron density sampled by the proton should be averaged over this space region around the channel axis. Taking into account that $k_c \approx 0.3$ (see Fig. 1), we obtain in our case that the average electron density of this region is only 3 per cent less than the average one. In conclusion we can say that close collisions are actually not so 'close', because k_c^{-1} is of the same order of the channel radius.

Another thing to remark is that the effect of channeling on plasmons excitations is of the same order of that due to close collisions, contrary to usual expectations. The total effect remains therefore ~ 1.3 per cent.

Our theoretical value for the energy loss in a random orientation is much lower than the experimental data, of about a factor 4.5, even if one takes into account the discrepancies among different experiments[20, 21]. This difference can be ascribed to the fact that we took into account only *s*-electrons, as we pointed out since the beginning.

However we can compare the relative decrease in stopping power due to channeling with experiments carried out in this laboratory

[22]. In these experiments the stopping power was measured as a function of the emergence angle. Each stopping power was correlated to a particular particle path along the channel and to the local electron density obtained by applying Poisson's equation to the interatomic potential.

The best fit with the experimental data was given by the following approximate relationship (see equation (7), Ref. [22]):

$$-\frac{dE}{dx} = 2.6 \times 10^8 \bar{Z} - 6.3 \times 10^7 (\bar{Z} - \bar{Z}_{loc}) \quad (14)$$

where $-(dE/dx)$ is in eV cm^{-1} , $\bar{Z}$ and $\bar{Z}_{loc}$ are the average and the local electron density respectively, in electron per atom*. For $(\bar{Z} - \bar{Z}_{loc})/\bar{Z} = 0.16$ a relative decrease in stopping power of 4 per cent is obtained from (14), which is not very different from the value found in this paper.

On the contrary we notice that in these experiments a decrease in electron density of ~ 55 per cent is associated with the best channeled particles. Such a variation cannot obviously be ascribed to s -electrons and treated by a nearly free electron model.

These are good reasons for extending our model to the tight-binding case. In fact both the results of the present calculations and the analysis of the experiments [22] show that to obtain detailed informations on valence elec-

tron density by channeling, more refinements, both in theory and experiments, are necessary.

REFERENCES

1. LINDHARD J., *Mat.-fys. Meddr.* **34**, N14 (1965).
2. SATTler A. R. and DEARNALEY G., *Phys. Rev. Lett.* **15**, 59 (1965).
3. ERGINSOY C., *Proc. Int. Conf. on Solid St. Phys. Res. with Accelerators, Brookhaven* (1967). BNL 50083 (C-52), 30.
4. APPLETON B. R., ERGINSOY C. and GIBSON W. M., *Phys. Rev.* **161**, 330 (1967).
5. BRICE D. K., *Phys. Rev.* **165**, 475 (1968).
6. LUTZ H. O., DATZ S., MOAK C. D. and NOGGLE T. S., *Phys. Rev. Lett.* **17**, 285 (1966).
7. MACHLIN E. S., *Phys. Lett.* **24A**, 173 (1967).
8. BONSIGNORI F. and DESALVO A., *Lett. Nuovo Cim.* **1**, 589 (1969).
9. ADLER S. L., *Phys. Rev.* **126**, 413 (1962).
10. FALK D. S., *Phys. Rev.* **118**, 105 (1960).
11. PINES D. and NOZIERES P., *The Theory of Quantum Liquids*, Vol. 1. Benjamin, New York (1966).
12. PENN D. R., *Phys. Rev.* **128**, 2093 (1962).
13. MACHLIN E. S., PETRALIA S., DESALVO A., MISSIROLI G. F. and ZIGNANI F., *Nuovo Cim.* **55B**, 263 (1968).
14. PHILLIPS J. C., *Solid State Physics*, Vol. 18, p. 55. Academic Press, New York (1966).
15. BRANDT W. and REINHEIMER J., *Can. J. Phys.* **46**, 607 (1968).
16. PINES D., *Elementary Excitations in Solids*, p. 176. Benjamin, New York (1963).
17. ENI FOO and HOPFIELD J. J., *Phys. Rev.* **173**, 635 (1968).
18. LINDHARD J. and WINTHER A., *Mat.-fys. Meddr.* **34**, N4 (1964).
19. BRANDT W. and REINHEIMER J., *Bull. Am. phys. Soc.* **13**, 1455 (1968).
20. WARSHAW S. D., *Phys. Rev.* **76**, 1759 (1949).
21. BADER M., PIXLEY R. E., MOZER F. S. and WHALING W., *Phys. Rev.* **103**, 32 (1956).
22. MACHLIN E. S., PETRALIA S., DESALVO A., ROSA R. and ZIGNANI F., *Phil. mag.* (In press).

* $\bar{Z}$ is obtained from the value of the stopping power in a random orientation and is equal to 8.25 electrons per atom.

OPTICAL PROPERTIES AND ELECTRONIC BAND STRUCTURES OF GROUP V AND IV-VI MATERIALS

P. J. LIN-CHUNG

Naval Research Laboratory, Wash. D.C. 20390 U.S.A.

(Received 17 November 1969; in revised form 31 December 1969)

Abstract—An evaluation of energy band calculations on group V and IV-VI semiconductors has been carried out with regard to the optical spectra which experimentally possess a striking structural similarity for this series of compounds. The interband transitions related to the optical reflectivity structure are assigned in a consistent manner from material to material. In this way, the general features of the energy bands along (100) and (110) directions may be determined in terms of four parameters, each of which is related to a reflectivity peak.

1. INTRODUCTION

EXPERIENCE with group V and IV-VI materials has shown that the fitting of optical spectra provides good criteria for the validity of band calculations. Other methods, namely, evaluation by means of the fitting of g factors and effective masses are restricted to small regions of the Brillouin zone and depend critically upon the possession of very accurate wave functions. In contrast, evaluation by means of the fitting of the optical spectra has validity throughout the Brillouin zone and has two levels of applicability. On the one hand, the positions of the optical structure depend upon the assignment of transition type and critical points obtained from the knowledge of the energy band structure. On the other hand, a knowledge of the wave functions allows an estimation of the intensities occurring in the optical spectra.

In recent years a considerable number of calculations (mostly by the pseudopotential method) of the electronic band structures of IV-VI compounds and group V elements have been carried out. These include the band structures of PbTe, PbSe, PbS, SnTe, As, Sb and Bi[1-11] the Fermi surface topologies of As and Sb[12, 5] and the electronic spectra

of SnTe and Sb[4, 13]. It seems worthwhile at this stage to evaluate these calculations with regard to the optical spectra which experimentally possess a striking structural similarity for this series of compounds. In order to do this in an orderly manner, we review the electronic properties of these crystallographically similar materials with particular emphasis on chemical shifts. Since the calculations of the electronic spectra of SnTe and Sb have already been analyzed with some care, we shall extrapolate from their structure to the other respective materials. Assisted further by bond and band arguments, we are able to determine the main features of the band structures along the (100) and (110) directions of these materials. We express these general features in terms of four parameters, each of which is related to a reflectivity peak in the electronic spectra. The common gross structure obtained for all these materials should be helpful in future calculations aimed at more detailed properties.

We begin, in the following section, with the general description of the structural and optical regularities among these substances. Subsequent sections will be devoted to the discussion of band structures and tran-

sition assignments to the optical spectra. Our proposed band model will be presented in Section 5.

2. THE STRUCTURAL AND OPTICAL REGULARITIES

As we have indicated previously, the group V and IV-VI semiconductors show a strong resemblance in their optical spectra and crystallographic structure. Simple cubic and closely related rhombohedral structures are favored by these materials which have average valency of five, just as the diamond and closely related hexagonal structures are favored by substances of average valence four. As a matter of fact, the chemical difference between the IV and VI atoms stabilizes the simple cubic structure; PbTe, PbSe and PbS are such examples. For smaller chemical difference between the two atoms in a unit cell, the simple cubic structure is unstable with regard to a small structural change. This change results in a small relative displacement of the two atoms in a face-centered-cubic unit cell along a body diagonal and a slight decrease of the rhombohedral angle from 60° . Thus, GeTe, As, Sb and Bi crystallize in rhombohedral structures. Further evidence of the instability of the simple cubic structure is provided by the phase transition from NaCl structure to rhombohedrally distorted structure for the alloys SnTe with GeSe or PbTe with GeTe [14].

The structure distortion is, indeed, small (e.g. the rhombohedral angles of arsenic and antimony are 54° and 57° compared with 60° in the cubic structure). It will, therefore, have very little influence on the overall band structures along the (100) and (110) directions. In a similar manner, most of the structure-dependent properties are expected to remain unaltered for such small structural changes.

We turn now to the optical properties. There has been a systematic survey of the optical reflectivity and absorption in the fundamental region of these materials at room temperature and at 77°K by Cardona and

Greenaway [15]. Each spectrum consists of six peaks [16]. An examination of the shapes of the reflectivity curves shows the striking resemblance among them. It is reasonable therefore to conclude that the corresponding peaks are caused by the same transition mechanism in each material.

The corresponding peak energies, in the case of the group V elements, decrease with increasing lattice parameter and atomic number. In the case of IV-VI compounds, they increase when the anion is replaced by lighter elements; a reverse trend is found when the cation is replaced by lighter elements. These facts confirm the conjecture that the shifts in peak energies are attributed not only to changes in the lattice parameter but also to core effects. The latter is even more pronounced in the high energy region of the spectra.

Previously, because of the lack of theoretical calculations on the spectra of these materials, these peaks were assigned intuitively to certain interband transitions. Detailed analysis in this paper leads to alternative assignments for all these transitions as will be discussed below.

Our assignments are such that corresponding peaks are caused by the same mechanism in each material.

The structural and optical similarities are particularly useful in obtaining an understanding of the band structures along the (100) and (110) directions for the following reasons. Firstly, a small rhombohedral distortion on the NaCl structure will lift the equivalency of the L and T points in the reciprocal space. The L and T points are the centers of the hexagons of the Brillouin zone faces perpendicular to the (111) and ($\bar{1}\bar{1}1$) directions, respectively. As a consequence, the band structure in the regions near L and T will be slightly altered whereas those along the (100) and (110) directions remain essentially unchanged for a small structural difference. It thus makes a comparison of the band structures of these materials along these

directions more meaningful. Secondly, the main reflectivity peaks (e.g. Sb and SnTe in Figs. 1 and 2) happen to be associated with the interband transitions along these two directions so that we do not lose much by confining our attention to these directions and their attendant optical spectra.

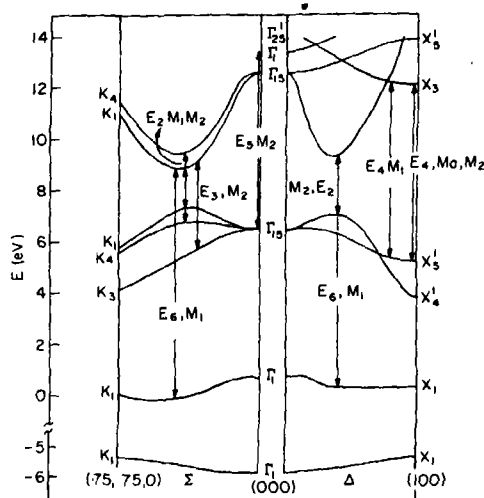


Fig. 1. The energy band structure of SnTe along the (100) and (110) directions (Ref. [4]).

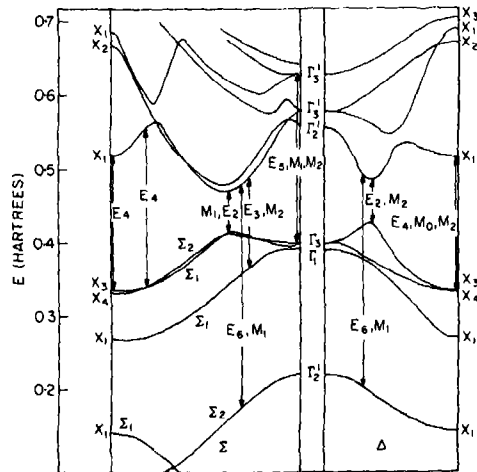


Fig. 2. The energy band structure of Sb along the ΓX and ΓKX directions. The lowest band in this figure is the second valence band (Ref. [5]).

3. BAND STRUCTURE CONSIDERATION

Consideration of the symmetry of the lattice alone has been of great help in interpreting the optical spectra. This is especially true in the determination of the interband transition selection rules and the critical points in the joint density of electronic states.

The joint density of states for interband transitions is defined by

$$J_{if}(\omega) = \frac{1}{8\pi^3} \int \frac{dS}{|\nabla(E_j - E_i)|_{E_j - E_i = \hbar\omega}}$$

The critical point occurs at k_0 when $|\nabla_k(E_j - E_i)|_{k=k_0} = 0$. A critical point is said to be of type M_0 if $E_j - E_i$ is a minimum at k_0 ; of type M_3 if $E_j - E_i$ is a maximum. If $E_j - E_i$ is a saddle point at k_0 , it is said to be of type M_1 when the effective mass at k_0 takes a positive value along one principal direction only and of type M_2 when the effective mass at k_0 takes positive values along two principal directions. The effective mass tensor at k_0 has components defined by $\hbar^{-1} \delta^2 E / \delta k_i \delta k_j$.

Symmetry alone requires the occurrence of critical points at symmetry points, along symmetry lines, or on symmetry planes; topological considerations related to connectivity, on the other hand, may force the existence of still more.

Indeed, for all crystals, the number of critical points is far greater than the number of reflectivity peaks observed. Consequently, group theoretical arguments alone are not selective enough and may sometimes lead to quite erroneous assignments of the reflectivity peaks. A knowledge of the optical properties thus requires a detailed knowledge of the electronic energy stages $E(k)$ and the wave function $\Psi(k)$ throughout the Brillouin zone. The computation of the electronic states throughout the Brillouin zone is a formidable self-consistent problem. Fortunately, a great deal of progress has been made in recent years through utilization of the semi-empirical pseudopotential method. In this section, the calculations of the band structures and optical

spectra of SnTe and Sb obtained in Refs. [4-6] using the local pseudopotential scheme [17] will be briefly summarized and an attempt will be made to extrapolate these results to the other materials.

In the pseudopotential scheme, the one electron energy eigenvalues can be obtained by solving the secular determinant.

$$\det |V(|\mathbf{k}-\mathbf{k}'|) + \left(\frac{\hbar^2 k^2}{2m} - E\right) \delta_{\mathbf{k}\mathbf{k}'}| = 0 \quad (1)$$

where $V(|\mathbf{k}-\mathbf{k}'|)$ represents the Fourier transform of the local pseudopotential. It can be expressed in terms of atomic pseudopotential form factors when there are two atoms per unit cell as follows.

$$V(\mathbf{g}) = V^{\text{IV}}(\mathbf{g}) + V^{\text{VI}}(\mathbf{g}) \cos(\mathbf{g} \cdot \boldsymbol{\zeta}), \boldsymbol{\zeta} \\ = \left(\frac{a}{2}, \frac{a}{2}, \frac{a}{2}\right) \text{ for IV-VI compounds} \quad (2)$$

$$V(\mathbf{g}) = V^{\text{V}}(\mathbf{g}) \cos\{2\pi u(h+k+l)\} \text{ for group V materials.}$$

The $V(\mathbf{g})$'s on the right-hand side of equation (2) are the atomic pseudopotential form factors for the group IV, VI, V elements, respectively, u is the internal displacement parameter in the rhombohedral structure and h, k, l are the components of $\mathbf{g}$ in the trigonal coordinate system [18]. The energy bands shown in Figs. 1 and 2 are the results of solving equation (1).

The optical spectra are determined from an evaluation of the imaginary part $\epsilon_2(\omega)$ of the complex dielectric function which is customarily calculated using a random phase approximation [19]. It then takes the following form.

$$\epsilon_2^u(\omega) = \left(\frac{2\pi e}{m\omega}\right)^2 \hbar \sum_{n,s} \int_{B.Z} \frac{2|M_{ns}^u(\mathbf{k})|^2}{(2\pi)^3} \delta(\omega_{ns}(\mathbf{k}) - \omega) d\Omega. \quad (3)$$

Here $|M_{ns}^u(\mathbf{k})|$ refers to the momentum matrix

element between states n and s and determines the oscillator strength of the transition, n designates the states with energies less than E_F , and s the states with energies greater than E_F . Also $\hbar\omega_{ns}(\mathbf{k}) = E_s(\mathbf{k}) - E_n(\mathbf{k})$.

In the computation of ϵ_2^u , the energy levels are sampled at a sufficiently large number of points in the primitive units of the Brillouin zone. (The primitive unit is $\frac{1}{12}$ th of the zone for the rhombohedral structure and $\frac{1}{48}$ th of the zone for the NaCl structure.) The spectral histograms with good statistics were then obtained and led to Figs. 3 and 4 [4, 13].

It should be noted that the semi-empirical pseudopotential used in these calculations employed the local approximation in the determination of the form factors and neglected spin-orbit interaction and other relativistic effects. This has led to considerable confusion and criticism in the literature concerning the validity and applicability of such a simple method in calculating electronic structures of heavier compounds. However, one may note from Figs. 3 and 4 that the calculated results are in reasonable agreement with experiment. We may understand this agreement in the following way. For one thing, it is clear that p -like states essentially derived from the anion do not have appreciable spin-orbit splitting. Further, states derived from the cation possessing some s -like character (possibly by mixing in the crystal) have reduced spin-orbit splitting relative to the free atom. Since it will turn out that it is just these states that are involved in the relevant interband transitions, it is reasonable to neglect spin-orbit effects. Moreover, relativistic effects are not important for most of the interband transitions under consideration. The E_g transition, which involves a low lying s state, is the only exception. Thus, we reach the conclusion that this simple scheme is adequate for our present purpose of elucidating the chemical shifts among these materials.

In general, there are many transitions associated with each structural feature in the spectrum and hence each such feature is, in general, related to more than one critical

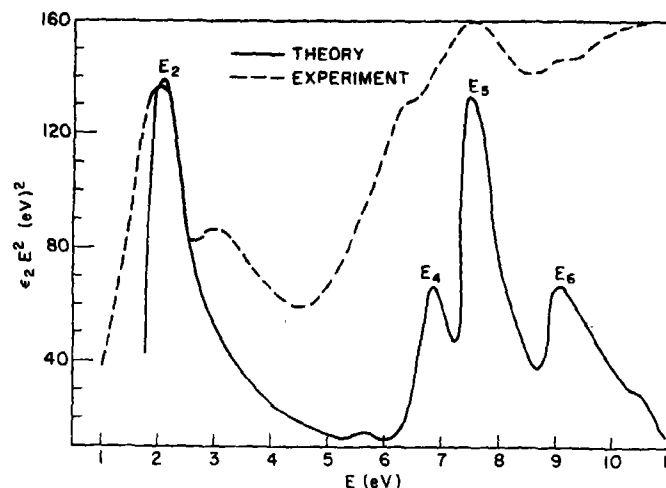


Fig. 3. The electronic spectrum of SnTe obtained theoretically (Ref.[4]) and experimentally (deduced from Ref.[15]).

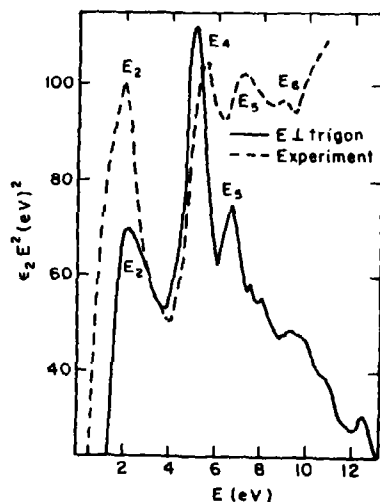


Fig. 4. The electronic spectrum of Sb. (Ref.[13]—The vertical scale of this figure in Ref.[13] is off by a factor of two, because of a drafting error.) The experimental data are from Ref.[15].

point in the band structure. The nature of these critical points can only be determined by an analysis of the interband energy contour diagram in k -space. This analysis has been carried out for SnTe in I. The results

are indicated in Fig. 1. On account of geometrical structural complications, a detailed analysis of the critical point types involved in the relevant transitions for antimony is a formidable task. Thus a comprehensive and exhaustive analysis of the spectrum to the degree that was achieved in the work on SnTe is not available. The transitions shown in Fig. 2 are therefore assigned primarily according to the oscillator strengths and energy gaps obtained in II. We will discuss their assignment more thoroughly in the next section. Also, we list the critical points in the first column of Tables 1 and 2 and discuss them more thoroughly in Section 4. The data listed in Table 1 are the experimental ones measured by Cardona and Greenaway [15].

4. TRANSITION ASSIGNMENTS

It follows from chemical bond arguments that for a structure with two atoms per unit cell possessing an inversion center at each atom, the wave functions can be classified as bonding and antibonding types. The former has no node along a nearest neighbor line whereas the latter has. As one moves away from the high symmetry points of the

Table 1(a). Proposed band parameters for IV-VI compounds. All entries are obtained experimentally in Ref. [15] (Energy units are in eV)

Transitions	PbS	PbSe	PbTe	SnTe
$4 \rightarrow 6 M_1 \Sigma_4 \rightarrow \Sigma_1$		3.3*		
E_2 $5 \rightarrow 6 M_2 \Delta_1 \rightarrow \Delta_1$	3.67	2.3* 3.12	3.0* 2.45	2.2* 2.07
$5 \rightarrow 7 M_1 \Sigma_1 \rightarrow \Sigma_4$			2.05*	
$4 \rightarrow 6 M_0 \}$ $X'_5 \rightarrow X_3$				
E_4 $5 \rightarrow 6 M_2 \}$	8.1	7.1	6.3	6.1
$4 \rightarrow 6 M_2$ between XK and ΓX				
$5 \rightarrow 10 M_2 \Gamma_{15} \rightarrow \Gamma'_{25}$				
E_5 $5 \rightarrow 9 M_1$ along KW on mirror plane near W	9.8	9.1	7.8	7.4
$2 \rightarrow 6 M_1 \Sigma_1 \rightarrow \Sigma_1$				
E_6 $2 \rightarrow 6 M_1 \Delta_1 \rightarrow \Delta_1$	13.9	12.5	11.2	9.1

*See Ref. [20].

Table 1(b). Proposed band parameters for GeTe and group V materials. All entries are obtained experimentally in Ref. [15] (Energy units are in eV)

Transitions	GeTe	As	Sb	Bi
$4 \rightarrow 6 M_1$ along ΓK				
E_2 $5 \rightarrow 6 M_2$ along ΓX	1.98	3.5	2.5	1.7
$5 \rightarrow 7 M_1$ along ΓK				
$4 \rightarrow 6 M_0 X_3 \rightarrow X_1$				
E_4 $5 \rightarrow 6 M_2 X_4 \rightarrow X_1$	5.4	6.9	5.7	5.0
$4 \rightarrow 6 M_2$ between ΓX and XK				
$5 \rightarrow 10 M_2 \}$ along ΓT close to Γ				
E_5 $5 \rightarrow 9 M_1 \}$	6.2	10.6	7.6	7.0
$2 \rightarrow 6 M_1$ along ΓX				
E_6 $2 \rightarrow 6 M_1$ along ΓK	7.8	13.6	9.4	8.6

Brillouin zone, one can see that the bonding characters as well as the atomic characters of the wave functions change gradually. In Fig. 1 the two lowest valence bands, which are completely occupied, are of s -bonding and s -antibonding natures, respectively. The Γ_{15} valence band is of p -bonding type, as are the X'_4 , X'_5 valence bands. However, the lowest conduction level at X , the X_3 , is predominantly d -bonding. The lowest conduction level at Γ , $\Gamma_{15}(2)$, on the other hand, is a p -antibonding

state. As for the lower symmetry points, the atomic character for the wave functions may be a mixed one. For example, consider the upper L_1 (or L_3) valence band. It is s -partially bonding (d partially bonding) about the group IV atom and p -partially bonding (p -partially bonding) about the group VI atom. One would therefore expect that, along the ΓL line, the atomic character of the wave functions should be a hybridized one.

As regards the arsenic type crystal, not

Table 2(a). Interband transitions obtained from previous theoretical calculations (All entries are in eV)

Transitions	PbS ^a	PbS ^b	PbSe ^a	PbSe ^b	PbTe ^a	PbTe ^b	PbTe ^c	SnTe ^b	SnTe ^h
4 → 6 $\Sigma_4 \rightarrow \Sigma_1$	4.76	3.5		3.2	2.31	2.0	2.04	1.95	2.5
5 → 6 $\Delta_1 \rightarrow \Delta_1$	3.54	3.4	2.99	2.8	2.04	2.2	4.03	2.2	2.2
5 → 7 $\Sigma_1 \rightarrow \Sigma_4$	2.72	3.7		3.2	2.31	2.3	2.45	2.0	1.7
4 → 6 $X_3^g \rightarrow X_3$		7.8		7.4		6.5			6.2
5 → 6 $X_3^g \rightarrow X_3$	7.07	7.5	6.94	7.0	5.98	5.9	5.73	6.81	5.8
5 → 10 $\Gamma_{15} \rightarrow \Gamma_{25}$	8.70	9.4	8.57	8.56	7.21	6.88	7.34	7.5	6.67
5 → 9 on mirror plane near W								7.13	
2 → 6 $\Sigma_1 \rightarrow \Sigma_1$	8.7				6.8	8.3	8.32	8.70	7.3
2 → 6 $\Delta_1 \rightarrow \Delta_1$	7.75		7.48		6.12	8.4	8.81	9.0	

^aSee Ref.[1].^bSee Ref.[4].^cSee Ref.[2] single group relativistic calculation.^hSee Ref.[3].

Table 2(b). Interband transitions obtained from previous theoretical calculations (All entries are in eV)

Transitions	GeTe ^b	As ^c	Sb ^d	Bi ^f	Bi ^g
4 → 6 along ΓK	1.6	1.99			2.50
5 → 6 along ΓX	1.4	1.99	2.0		0.49
5 → 7 along ΓK	1.5	2.75	2.4		
4 → 6 $X_3 \rightarrow X_1$	6.3	4.24	5.1	4.42	3.54
5 → 6 $X_4 \rightarrow X_1$	5.9	4.68	5.8	5.66	5.17
5 → 10 } along ΓT	6.8		6.8	6.71	5.03
5 → 9 }					
2 → 6 along ΓX	7.8	6.69	8.16		8.97
2 → 6 along ΓK		7.48	8.16		8.97

^cSee Ref.[9].^dSee Ref.[13].^fSee Ref.[10].^gSee Ref.[11].^hSee Ref.[3].

only the atomic character but also the bonding character has been mixed slightly due to the small structural distortion.

Accordingly, the optical spectra can be analyzed into three groups. The E_2 peak belongs to the first group which is associated with transitions between p -bonding and p -antibonding states. These states are less

affected by hybridization of s -like states and have predominantly p characters. The second group is comprised of E_4 and E_5 peaks, which are associated with transitions between p -bonding and d -bonding states. In group IV elements, Si and Ge, the d -bonding states lie way above the conduction band edge. Hence their oscillator strength should be smaller due to loosely bonding behavior of d states. The absence of the E_4 and E_5 peaks in the spectra of group IV elements may therefore be thought of as a direct consequence of this smaller oscillator strength. The third group consists only of the E_6 peak. The related transitions connect the low-lying s -like cation levels in the valence band and the antibonding p levels in the conduction band just above E_F . We exclude the discussion of the E_1 and E_3 peaks in this paper mainly for the reason that the E_1 transitions do not happen in the two directions under consideration and the identification of the E_3 transition has not yet been soundly established.

In the following we shall describe in turn the critical points relating to the optical absorption peaks. (1) E_2 : The $4 \rightarrow 6$, $5 \rightarrow 6$, $5 \rightarrow 7$ transitions ($4 \rightarrow 6$ means the transition

between 4th and 6th bands) in SnTe and Sb all contribute to the E_2 peaks. In SnTe it has been shown that they are of M_1 , M_2 , and M_1 type edges at points along ΓK , ΓX and ΓK directions, respectively[4]. Our analysis about the E_2 is further evidenced by recent electroreflectance measurements[20] which prove that the structure at 2.05 eV (2.3 eV) in the spectrum of PbSe (PbS) belongs to M_1 transition whereas the structure at 2.2 eV in PbTe and the structure above 3 eV in PbSe and PbS are caused by M_2 transitions. As mentioned in II, the E_2 peak in Sb arises from points near (0.59, -0.43, 0.08) which is near the ΓK direction. Therefore we tentatively assigned E_2 to be due to the transitions near or at the directions of ΓK and ΓX as listed in Table 2. We assume the same situation applies for the other IV-VI and group V materials. (2) E_3 : Although in the joint density of states curve of SnTe there is a small peak at the energy $E = E_3$, this peak does not show up in both Figs. 3 and 4. The exceedingly small oscillator strengths are believed to be responsible for this. It is known that the oscillator strengths, calculated from pseudowavefunctions inherent some uncertainties from the pseudopotential method, we prefer not to choose this peak as a parameter in the determination of our proposed band structures. We only want to point out that E_3 structure is believed to be of M_1 type transition[20]. (3) E_4 and E_5 peaks: These peaks belong to the interband transitions 4, 5 $\rightarrow$ 6 and 5 $\rightarrow$ 10 at X and Γ , respectively. For the NaCl structure, the lowest X'_5 and X_3 levels have the same energy in the free electron case, as do the lowest Γ_{15} and Γ'_{25} levels. Thus, interactions between each of these levels and other levels having the same irreducible representations may be ignored when we estimate the splittings of X'_5 , X_3 and Γ_{15} , Γ'_{25} due to the presence of weak pseudopotentials. As these splittings characterize the E_4 , E_5 transitions, we have

$$E_4 = E(X_3) - E(X'_5) = 2(V_{220} - V_{200}) \quad (4)$$

$$E_5 = E(\Gamma'_{25}) - E(\Gamma_{15}) = 2(V_{222} - V_{200}). \quad (5)$$

Here V_k represents the Fourier transform of the pseudopotentials. Examining the pseudopotential form factors deduced in ref.[1] for the lead salts, we see that the E_4 and E_5 transitions, given by equations (4) and (5), increase as one goes from PbTe to PbS, which is consistent with the experimental results shown in Table 1. From this estimation it follows that these two peaks should indeed be assigned as due to two different transitions between p -bonding and d -anti-bonding states instead of a spin-orbit doublet [15].

Two other critical points have been found to contribute to the E_4 , E_5 peaks in SnTe. They are points between XK and ΓX directions and along KW on the mirror plane near W .

For As-type crystals the E_5 critical point moves to a point along the ΓT direction close to Γ , due to the structural distortion. (4) E_6 peak: the E_6 peak in SnTe was analyzed as composed of two critical points along the ΓK and ΓX directions. These are the transitions between the low-lying core levels and the conduction level just above Fermi level i.e., the 2 $\rightarrow$ 6 transition. It is known that the oscillator strength obtained from the plane wave part of the valence wave functions underestimates the core effect which is particularly important for low-lying levels. The disappearance of the E_6 peak in the calculated Sb spectrum may be attributed to the underestimation of the oscillator strength. However, we note that in Sb, along the ΓK and ΓX directions, we can still find two critical points of the 2 $\rightarrow$ 6 transition which have energy approximately equal to 8.16 eV[13] compared with the observed value 9.4 eV.

5. PROPOSED BAND STRUCTURES

We list the interband transitions in the existing calculations in Table 2. The values for Sb and SnTe shown in Table 1 are in very good agreement with those in Table 2.

The values for PbTe, PbSe, PbS in Table 2 give the chemical shifts predicted by experiment. Apart from the E_6 , all values deviate from experiment by a few tenths of an eV. The E_6 peak depends strongly on the relativistic effect and is difficult to obtain accurately. Note that the E_6 , listed in Table 2 for the lead salts, appear to be too small. This indicates that the s -shift effect on the second band might be overestimated in previous calculations. The second band is essentially an anion s orbital and was deliberately placed relative to the conduction band Γ_{15} in Ref.[1] such that the gap $\Gamma_1(2) \rightarrow \Gamma_{15}(2)$ equals E_4 of Table 1. As we now recognize that the $\Gamma_1(2) \rightarrow \Gamma_{15}(2)$ transition is not responsible for the E_4 peak, previous calculations may be modified to yield larger E_6 values. Subsequent relativistic *OPW* calculations by Herman *et al.* [3] also give a small value of E_6 for PbTe. Furthermore, in their calculation, no critical points appear in the ΓK or ΓX directions for the $2 \rightarrow 6$ transition in PbSe and PbS. Unless a future first principle calculation on the optical spectra of the lead salts proves the assignment of the critical points related to the E_6 peak to be different from that for SnTe, it is likely that the position of the second band at Γ in a more realistic energy band picture should be higher than the ones appearing in previous works. A reduction of the relativistic s -shift effect on the anion s orbital may accomplish this.

The *OPW* calculation of As[9], as shown in Table 2, has also turned out relatively smaller values for the E_2 , E_4 , and E_8 peaks.

The relativistic pseudopotential calculation [11] and the relativistic *APW* calculation [10] on Bi seem to produce quite good agreement with experiment, except that the $5 \rightarrow 6$ transition at the critical point along ΓX and the transition $5 \rightarrow 10$ along ΓT appear to be too small.

Based on the above analysis, we propose a general feature of the energy bands along the (100) and (110) directions. As displayed in Figs. 5 and 6, they may be characterized

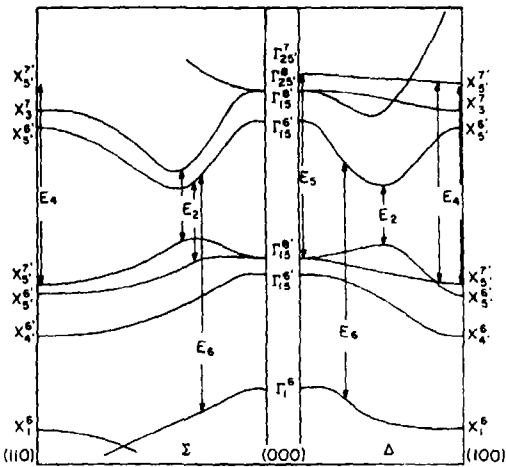


Fig. 5. A qualitative sketch of the proposed energy band structures of IV-VI compounds.

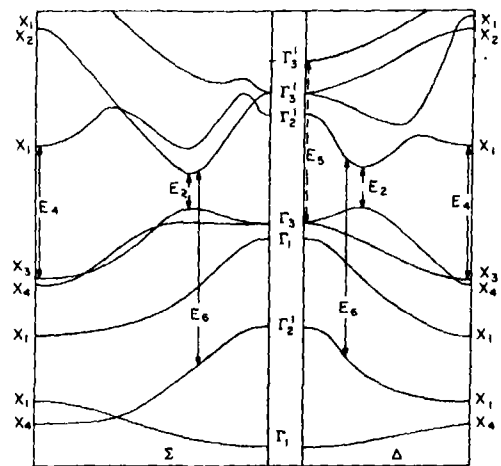


Fig. 6. A qualitative sketch of the proposed energy band structures of group V materials and GeTe.

by four parameters; E_2 , E_4 , E_5 , E_6 . Our proposed band model is strongly suggested by simultaneous examination of the direct band gap in isoelectronic sequences of IV-VI and V materials as well as by the bond and band arguments. The four parameters determine the common gross structure of the optical spectra derived from the calculated bands. Use of the parameters listed in Table

I therefore insure that the calculated optical spectra will be coincident with the experimental observations and provides a foundation for future calculations on these materials designed to obtain more detailed results.

Acknowledgements—The author is very grateful to Drs. R. F. Wallis and S. Teitler for their helpful discussion on the manuscript.

REFERENCES

1. LIN P. J. and KLEINMAN I., *Phys. Rev.* **142**, 478 (1966).
2. CONKLIN J. B. Jr., JOHNSON L. E. and PRATT G. W. Jr., *Phys. Rev.* **137**, A1282 (1965).
3. HERMAN F., KORTUM R. L., ORTENBURGER I. B. and VAN DYKE J. P., to be published in *J. Phys.* (IV-VI Colloquium Supplement).
4. LIN P. J., SASLOW W. and COHEN M. L., *Solid State Commun.* **5**, 893 (1967). (Hereafter referred to as I).
5. FALICOV L. M. and LIN P. J., *Phys. Rev.* **141**, 562 (1966).
6. FALICOV L. M. and GOLIN S., *Phys. Rev.* **137**, A871 (1965).
7. COHEN M. H., FALICOV L. M. and GOLIN S., *IBM J. Res. Devel.* **8**, 215 (1964).
8. RABII S., *Phys. Rev.* **167**, 801 (1968).
9. GOLIN S., *Phys. Rev.* **140**, A993 (1965).
10. FERREIRA L. G., *J. Phys. Chem. Solids* **28**, 1897 (1967).
11. GOLIN S., *Phys. Rev.* **166**, 643 (1968).
12. LIN P. J. and FALICOV L. M., *Phys. Rev.* **142**, 441 (1966).
13. LIN P. J. and PHILLIPS J. C., *Phys. Rev.* **147**, 469 (1966). (Hereafter referred to as II).
14. NIKOLIC P. M., *Br. J. appl. Phys.* **16**, 1075 (1965); WOOLLEY J. C. and NIKOLIC P. M., *J. electrochem. Soc.* **112**, 82 (1965).
15. CARDONA M. and GREENAWAY D. L., *Phys. Rev.* **133**, A1685 (1964).
16. The spectra for Sb, SNTe and GeTe represent exceptions to this observation since in these cases the lowest energy peak E_1 does not appear.
17. The local pseudopotential scheme ignores the momentum and energy dependence of pseudopotential.
18. For a complete description of the trigonal coordinate system in Bi structure, see ref.[6].
19. COHEN M. H., *Phil. Mag.* **3**, 762 (1958).
20. ASPNES D. E. and CARDONA M., *Phys. Rev.* **173**, 714 (1968).

A POSSIBILITY OF ORTHORHOMBIC JAHN–TELLER DISTORTION

SHINJI MURAMATSU and TAKESHI IIDA

Department of Physics, Faculty of Science, Osaka City University, Osaka, Japan

(Received 18 August 1969; in revised form 29 December 1969)

Abstract—A possibility has been investigated that an octahedral complex, having sufficiently isolated triply degenerate electronic state, undergoes an orthorhombic distortion through Jahn–Teller effect linear and quadratic in vibrational T_2 mode. Effects of vibrational E mode are assumed to be small compared with those of T_2 mode and are neglected. The inclusion of the quadratic effects leads to the stable potential minima which stabilize the orthorhombic distortion for suitable conditions.

1. INTRODUCTION

SINCE in 1937 Jahn and Teller[1] proved the theorem concerning to the intrinsic instability of any nonlinear complex, the electronic state of which was orbitally degenerate, many authors[2] have investigated stable configuration of nonlinear complexes. Taking account of linear vibronic interaction, Öpik and Pryce[3] have shown that an octahedral complex having a triply degenerate ground state may distort to a pure tetragonal or trigonal configuration. In their investigation, the linear interaction contains both E and T_2 vibrational modes. When only T_2 mode is taken into account, the stable configuration turns out to be a pure trigonal distortion; the extremal energy value associated with the orthorhombic point ($-A^2/2\beta$) is always higher than that with the trigonal point ($-2A^2/3\beta$).* Recently Wysling and Müller[4] have shown the same result in more detail. In these studies, however, detailed discussions have not been given to effects of quadratic terms of the vibronic interaction.

In our present work, the quadratic effects are investigated in more detail for a particular case where T_2 vibronic interactions are larger than E vibronic interactions which are assumed to be small and ignored. The effects

quadratic in normal coordinates arise from the quadratic coupling, treated to first order perturbation theory, and the linear coupling to a distant electronic level, treated to second order. If the spacing of the electronic levels is not large compared with the vibronic interactions, the above treatment is not applicable. Such a situation has recently been investigated by Stoneham and Lannoo[5]. They have discussed the effects of the linear coupling for two nearly degenerate levels.

In Section 2, we calculate energy values at extremal points with respect to nuclear coordinates by Öpik and Pryce's procedure[3]. In Section 3, we discuss the conditions for occurrence of the orthorhombic Jahn–Teller distortion. We will show that introduction of the quadratic terms makes it possible that the octahedral complex having a triply degenerate ground state distorts to the orthorhombic configuration.

In the study of electron paramagnetic resonance attributed to S^- ion in some alkali-halides, Vannotti and Morton observed anisotropic g tensor which was orthorhombic[6]. They suggested a few mechanisms to explain the origin of the anisotropy, one being Jahn–Teller distortion. A direct comparison, however, is not established in this paper between our suggestion and their experiment; it will be put forward by more detailed analysis experimentally and theoretically.

*The notation A corresponds to B in the paper of Öpik and Pryce.

2. EVALUATION OF EXTREMAL ENERGY

In this section, we calculate energy values with respect to the extremal points in nuclear coordinate space. The Hamiltonian of a given system is

$$H = H_e(\mathbf{r}, Q) + T_N. \quad (2.1)$$

The first term contains two types of energy: the kinetic energy of electrons and all Coulomb interactions between electrons and nuclei. In the parentheses, $\mathbf{r}$ represents the coordinates of electrons $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n$; Q stands for a set of normal coordinates of nuclei. The second term is the kinetic energy of nuclei.

In the adiabatic approximation, a vibronic eigenfunction of the Hamiltonian (2.1) usually may be written in a form

$$\phi(\mathbf{r}, Q) = \varphi(\mathbf{r}, Q)\zeta(Q). \quad (2.2)$$

An electronic wavefunction $\varphi(\mathbf{r}, Q)$ depends parametrically on Q and satisfies the Schrödinger equation

$$H_e(\mathbf{r}, Q)\varphi_\alpha(\mathbf{r}, Q) = \epsilon_\alpha(Q)\varphi_\alpha(\mathbf{r}, Q), \quad (2.3)$$

where α denotes the electronic quantum number. The wavefunction $\varphi_\alpha(\mathbf{r}, Q)$ is normalized under integration over $\mathbf{r}$ alone:

$$\int |\varphi_\alpha(\mathbf{r}, Q)|^2 d\mathbf{r} = 1. \quad (2.4)$$

A vibrational wavefunction $\zeta(Q)$ satisfies the vibrational Schrödinger equation

$$[T_N + \epsilon_\alpha(Q)]\zeta_{av}(Q) = E_{av}\zeta_{av}(Q). \quad (2.5)$$

where v labels a vibrational state. In this equation $\epsilon_\alpha(Q)$ acts as a potential for the nuclear motion.

We assume that $H_e(\mathbf{r}, Q)$ can be expanded in a Taylor series of Q about a symmetrical configuration, $Q = 0$. Ignoring anharmonic terms higher than second order in Q , we obtain

$$H_e(\mathbf{r}, Q) = H_e(\mathbf{r}, 0) + H_e^{(1)}(\mathbf{r}, Q) + H_e^{(2)}(\mathbf{r}, Q),$$

where

$$H_e^{(1)}(\mathbf{r}, Q) = \sum_{ak} U_{ak}(\mathbf{r})Q_{ak}$$

and

$$H_e^{(2)}(\mathbf{r}, Q) = \frac{1}{2} \sum_{ak} \sum_{\beta l} U_{ak,\beta l}(\mathbf{r})Q_{ak}Q_{\beta l}.$$

α and β denote irreducible representations according to which the normal coordinates are characterized; k and l their components.

We regard $H_e^{(1)}$ and $H_e^{(2)}$ as perturbations to the pure electronic part $H_e(\mathbf{r}, 0)$. The effects of vibronic interactions are taken into account to quadratic in nuclear coordinates; the effects of $H_e^{(1)}$ and $H_e^{(2)}$, treated to the accuracy of first order perturbation theory, and the ones arising from linear coupling $H_e^{(1)}$ to a distant level, treated to second order. The effective interaction Hamiltonian can be written as

$$H'_e = \sum_{ak} U_{ak}Q_{ak} + \frac{1}{2} \sum_{ak} \sum_{\beta l} U_{ak,\beta l}Q_{ak}Q_{\beta l} - \frac{1}{\delta} \sum_m \sum_{ak,\beta l} U_{ak}|m\rangle \langle m| U_{\beta l}Q_{ak}Q_{\beta l}, \quad (2.6)$$

where δ is the energy separation between a ground level and a lowest excited level which can couple with the ground level through the linear interaction $H_e^{(1)}$; the sum over m is taken in the manifold of the excited level. In this expression, we take into account of the lowest excited level, assuming that other excited levels are lying in much higher energy.

The above treatment is available to the case where the spacing of the electronic levels is sufficiently large compared with the vibronic interactions. If such a condition is violated, we must treat the problem by other method such as Stoneham and Lannoo[5] have recently discussed.

In the following, we assume that the Hamiltonian $H_e(\mathbf{r}, 0)$ possesses octahedral symmetry and gives an orbital triplet ground state; in the vibronic interaction Hamiltonians, only T_2 mode is to be dominant and

the effects of the other modes are so small as to be neglected. An orbital triplet state in octahedral symmetry belongs to the three-dimensional irreducible representation T_1 or T_2 . The three components of the electronic state transform as x, y, z , respectively, if the irreducible representation under consideration is T_1 , and as yz, zx, xy , respectively, if it is T_2 . A_2 (or A_1), E , T_1 and T_2 levels can couple with the ground level T_1 (or T_2) through the linear vibronic interaction $H_e^{(1)}$ since $H_e^{(1)}$ has the symmetry of T_2 . We, therefore, take into account of the four cases such as (T_1, A_2) , (T_1, E) , (T_1, T_1) and (T_1, T_2) ,* where the first letter in parentheses indicates the symmetry of the ground level and the second the symmetry of the lowest excited level.

For these four cases, the effects of vibronic interactions can be found by solving the secular equation of the effective Hamiltonian H_e' within the manifold of orbital triplet T_1 :

$$\begin{aligned} & \left[\frac{1}{2}[(2B - 3K_2)Q_\xi^2 - (B + 3K_1)(Q_\eta^2 + Q_\zeta^2)] \right. \\ & \left. AQ_\xi + (B' + K_3)Q_\xi Q_\eta \right. \\ & \left. AQ_\eta + (B' + K_3)Q_\xi Q_\zeta \right. \\ & \left. AQ_\zeta + (B' + K_3)Q_\xi Q_\eta \right. \\ & \left. AQ_\xi + (B' + K_3)Q_\xi Q_\zeta \right. \\ & \left. \frac{1}{2}[(2B - 3K_2)Q_\zeta^2 - (B + 3K_1)(Q_\eta^2 + Q_\xi^2)] \right] \begin{bmatrix} a_1 \\ a_2 \\ a_3 \end{bmatrix} \\ & + \frac{1}{2}\beta(Q_\xi^2 + Q_\eta^2 + Q_\zeta^2) \cdot I \cdot \begin{bmatrix} a_1 \\ a_2 \\ a_3 \end{bmatrix} = \epsilon(Q) \cdot I \cdot \begin{bmatrix} a_1 \\ a_2 \\ a_3 \end{bmatrix}, \end{aligned} \quad (2,7)$$

where I is a three dimensional unit matrix; A a linear coupling coefficient after integration with respect to electron coordinates; Q_ξ, Q_η, Q_ζ are normal coordinates of T_2 ; B, B' quad-

ratic coupling coefficients. The detailed expressions of K_1, K_2 and K_3 are given for the four cases in Table 1, where C_i ($i = 1, 2, 3, 4$) are appropriate linear coupling coefficients.

Table 1. The detailed expressions of K_1, K_2 and K_3 for four cases (T_1, A_2) , (T_1, E) , (T_1, T_1) and (T_1, T_2) . C_i is an appropriate linear coupling coefficient; δ_i an energy separation between the ground level and a lowest excited level

	(T_1, A_2)	(T_1, E)	(T_1, T_1)	(T_1, T_2)
K_1	0	0	C_3^2/δ_3	C_4^2/δ_4
K_2	C_1^2/δ_1	C_2^2/δ_2	0	0
K_3	0	$C_2^2/2\delta_2$	$-C_3^2/\delta_3$	C_4^2/δ_4

The expression $(1/2)\beta(Q_\xi^2 + Q_\eta^2 + Q_\zeta^2)$ is usually referred to a quasi-elastic potential. The eigenfunction $\varphi_a(\mathbf{r}, Q)$ of equation (2,3) can be expressed as a linear combination of unperturbed eigenfunctions in this approximation. The normalization condition for $\varphi(\mathbf{r}, Q)$ yields

$$a_1^2 + a_2^2 + a_3^2 = 1, \quad (2,8)$$

where a_i ($i = 1, 2, 3$) are assumed to be real[3-4].

For simplicity, we express equation (2,7) symbolically as

$$W\mathbf{a} + V\mathbf{a} = \epsilon\mathbf{a}, \quad (2,7')$$

where $W\mathbf{a}$ stands for the first term on the left hand side of equation (2,7) and $V\mathbf{a}$ for the second.

It is difficult to find energy, $\epsilon(Q)$, itself. Instead, we attempt to find, in the normal coordinate space (Q -space), those points at which the energy $\epsilon(Q)$ takes extremal values and then to find the extremal energy values themselves. The relations of Q and $\mathbf{a}$ to be satisfied at the extremal points in Q -space are

*When the ground level has the symmetry of T_2 , four cases (T_2, A_1) , (T_2, E) , (T_2, T_1) and (T_2, T_2) should be discussed. In what follows, we take up only the case where the ground level has the symmetry of T_1 .

$$\bar{\mathbf{a}} \frac{\partial W}{\partial \bar{Q}_k} \mathbf{a} + \frac{\partial V}{\partial Q_k} = 0, \quad (k = \xi, \eta, \zeta), \quad (2,9)$$

where $\bar{\mathbf{a}}$ is a transpose of $\mathbf{a}$. Rewriting equation (2,9) in full expression, we obtain

$$\begin{aligned} & [(B + K_1 - K_2)a_1^2 - \frac{1}{2}(B + 3K_1) + \beta]Q_\xi \\ & + (B' + K_3)a_1a_2Q_\eta + (B' + K_3)a_3a_1Q_\zeta \\ & = -Aa_2a_3, \\ & (B' + K_3)a_1a_2Q_\xi + [(B + K_1 - K_2)a_2^2 \\ & - \frac{1}{2}(B + 3K_1) + \beta]Q_\eta + (B' + K_3)a_2a_3Q_\zeta \\ & = -Aa_3a_1, \\ & (B' + K_3)a_3a_1Q_\xi + (B' + K_3)a_3 \\ & + (B' + K_3)a_3a_1Q_\xi + (B' + K_3)a_3a_2Q_\eta \\ & + [(B + K_1 - K_2)a_3^2 - \frac{1}{2}(B + 3K_1) + \beta]Q_\zeta \\ & = -Aa_1a_2. \end{aligned} \quad (2,10)$$

These equations can be regarded as a system of linear inhomogeneous equations in Q_k [4]. The solutions, which we denote $\bar{Q}_k$, are the coordinates of extremal points of the energy surface in Q -space. The solutions of the simultaneous equations (2,10) are expressed as follows:

$$\begin{aligned} \bar{Q}_\xi = & -\frac{3Aa_2a_3}{(B + 3K_1)\Delta} \\ & \times \left\{ X^2 + \frac{3}{(B + 3K_1)}[(B + K_1 - K_2) \right. \\ & - (B - 2B' + K_1 - K_2 - 2K_3)a_1^2]X \\ & + \frac{9(B' - B - K_1 + K_2 + K_3)}{(B + 3K_1)^2} \\ & \times [(B' + K_3)(a_1^2a_2^2 + a_3^2a_1^2 - a_2^2a_3^2) \\ & \left. - (B + K_1 - K_2)a_2^2a_3^2] \right\}, \end{aligned} \quad (2,11)$$

where $X = [3\beta/2(B + 3K_1)] - 1$ and Δ is the coefficient determinant of equation (2-10). The expressions of $\bar{Q}_\eta$ and $\bar{Q}_\zeta$ are given by cyclic permutations of subscripts 1, 2, 3.

We now discuss these solutions for three cases, (1), (2) and (3).

Case (1). $a_1 \neq 0, a_2 \neq 0, a_3 \neq 0$

Substituting the expressions $\bar{Q}_\xi, \bar{Q}_\eta, \bar{Q}_\zeta$ given in equation (2,11) in the corresponding coordinates of the eigenvalue equation (2,7), respectively, we can easily obtain the relation $a_1^2 = a_2^2 = a_3^2$. From this relation and the normalization condition (2,8), the eigenvectors $\mathbf{a}$ at extremal points in Q -space are found to be fourfold:

$$(a_1, a_2, a_3) = (3)^{-1/2}(1, 1, 1); \quad (2,12a)$$

$$= (3)^{-1/2}(-1, 1, 1); \quad (2,12b)$$

$$= (3)^{-1/2}(1, -1, 1); \quad (2,12c)$$

$$= (3)^{-1/2}(1, 1, -1). \quad (2,12d)$$

From equation (2,12) and the expressions of $\bar{Q}_k$, we obtain the coordinates of extremal points in Q -space as

$$\bar{Q}_1 = (\bar{Q}_\xi, \bar{Q}_\eta, \bar{Q}_\zeta) = (-q, -q, -q); \quad (2,13a)$$

$$= (-q, q, +q); \quad (2,13b)$$

$$= (q, -q, +q); \quad (2,13c)$$

$$= (q, q, -q), \quad (2,13d)$$

where $q = 2A/[3\beta + 4B' - 2(2K_1 + K_2 - 2K_3)]$. These four sets of coordinates in Q -space correspond to trigonal distortion of octahedral complex. The eigenvalue $\epsilon(\bar{Q}_1)$ at these extremal points are easily found to be

$$\epsilon(\bar{Q}_1) = -\frac{2A^2}{3\beta + 4B' - 2(2K_1 + K_2 - 2K_3)}. \quad (2,14)$$

If quadratic terms become negligible small compared with the quasielastic constant β , i.e. $B/B \rightarrow 0$ and $K_i/\beta \rightarrow 0$ ($i = 1, 2, 3$), then the value of q tends to $2A/3\beta$ and extremal energy $\epsilon(\bar{Q}_1)$ to $-2A^2/3\beta$. Öpik and Pryce find the coordinates of extremal points and extremal energy values only with the linear terms

of T_2 and E modes included [3]. If E mode is excluded their results agree with our limiting values obtained above.

Case (2). $a_1 \neq 0$, $a_2 \neq 0$, $a_3 = 0$

In this case, we have three equivalent cases, one of which is being discussed. In a manner similar to case (1), we obtain the relation $a_1^2 = a_2^2$. From this relation and the normalization condition (2,9), the eigenvectors $\mathbf{a}$ at the extremal point in Q -space are found as follows:

$$(a_1, a_2, a_3) = (2)^{-1/2}(1, 1, 0); \quad (2,15a)$$

$$= (2)^{-1/2}(1, -1, 0). \quad (2,15b)$$

The coordinates of the extremal points corresponding to the above eigenvectors can be obtained from equation (2,11) as

$$\begin{aligned} \bar{Q}_{II} &= (\bar{Q}_\epsilon, \bar{Q}_\eta, \bar{Q}_t) \\ &= \left(0, 0, \mp \frac{3A}{3\beta - 2(B + 3K_1)}\right), \end{aligned} \quad (2,16)$$

where the upper and lower signs correspond to (2,15a) and (2,15b), respectively. The two sets of coordinates in Q -space lead to orthorhombic distortion of an octahedral complex.

The secular equation (2,7) generally has three eigenvalues at a point in Q -space, which are lying on three sheets of energy surface. Let us concern only with one of the two extremal points (2,16), e.g. the one with plus sign. We will later find it necessary to have two excited states at the extremal point as well as the extremal energy itself. The secular equation (2,7) is to be solved at the point $\bar{Q}_{II} = (0, 0, 3A/[3\beta - 2(B + 3K_1)])$. The energy eigenvalues and corresponding eigenvectors at this point are given as follows:

$$a_2 = (2)^{-1/2} \begin{bmatrix} 1 \\ 1 \\ 0 \end{bmatrix}, \quad \epsilon_2(\bar{Q}_{II}) = \frac{9A^2/2}{3\beta - 2(B + 3K_1)}, \quad (2,17a)$$

$$a_1 = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}, \quad \epsilon_1(\bar{Q}_{II}) = \frac{(3A^2/2)(4B - 6K_2 + 3\beta)}{3\beta - 2(B + 3K_1)^2}, \quad (2,17b)$$

$$a_0 = (2)^{-1/2} \begin{bmatrix} 1 \\ -1 \\ 0 \end{bmatrix}, \quad \epsilon_0(\bar{Q}_{II}) = -\frac{3A^2/2}{3\beta - 2(B + 3K_1)}. \quad (2,17c)$$

If the quadratic effects can be ignored compared with the quasielastic constant β , i.e. $B/\beta \rightarrow 0$ and $K_1/\beta \rightarrow 0$, then the coordinate of the extremal point becomes $(0, 0, A/\beta)$ and the extremal energy $\epsilon_0(\bar{Q}_{II})$ to $-A^2/2\beta$. This limiting case corresponds to the one discussed by Öpik and Pryce [3], who take into account only the linear terms.

Case (3). $a_1 \neq 0$, $a_2 = a_3 = 0$

In this case, we have two more equivalent cases that are given by cyclic permutations of subscripts 1, 2, 3. This case is physically uninteresting since the extremal point is $\bar{Q}_\epsilon = \bar{Q}_\eta = \bar{Q}_t = 0$ and from the secular equation (2,7) we have $\epsilon(\bar{Q}_{III}) = 0$.

Before leaving this section, we note that case (1) and case (2) lead to trigonal and orthorhombic distortion at their extremal points, respectively, while case (3) keeps the octahedral complex to remain totally symmetric at its own extremal point. We will, therefore, discard case (3) in the following section.

3. CONDITIONS FOR ORTHORHOMBIC DISTORTION

In this section, we will discuss the conditions for the occurrence of orthorhombic Jahn-Teller distortion. It becomes possible to expect orthorhombic Jahn-Teller distortion, if the following conditions are satisfied:

(a) the extremal energy value $\epsilon_0(\bar{Q}_{II})$ is lower than another one $\epsilon(\bar{Q}_I)$, i.e. $\epsilon_0(\bar{Q}_{II}) < \epsilon(\bar{Q}_I)$,

(b) the energy surface is stable at the point $\bar{Q}_{II}$ in Q -space.

Using equations (2,14) and (2,17) and can-

celling common factors, we can replace the condition (a) simply by

$$B' > -\frac{3}{4}B + \left(\frac{\beta}{4} - K_1 + \frac{1}{2}K_2 - K_3\right), \quad (3.1)$$

provided that the denominators in equations (2.14) and (2.17c) are positive, i.e.

$$B' > -\frac{3}{4}B + (-\frac{3}{4}\beta - K_1 + \frac{1}{2}K_2 - K_3), \quad (3.2a)$$

and

$$B < \frac{3}{2}\beta - 3K_1. \quad (3.2b)$$

If either of the conditions (3.2a), (3.2b) is violated, it is easy to show that the system is unstable to an infinite distortion. It is to be noted that the inequality (3.2a) is automatically satisfied in the region determined by the inequalities (3.1) and (3.2b). A further condition bounding unstable region is obtained from the instability associated with the state (2.17b), being

$$B > -\frac{3}{4}B + \frac{3}{2}K_2. \quad (3.3)$$

If increment in energy $\epsilon_0(\bar{Q}_{II} + \mathbf{x}) - \epsilon_0(\bar{Q}_{II})$ associated with an arbitrary increment $\mathbf{x} = (x_\epsilon, x_\eta, x_t)$ from the extremal point $\bar{Q}_{II}$ is positive, then the extremal point $\bar{Q}_{II}$ is stable on the energy surface. According to Öpik and Pryce's procedure[3], the energy increment can be calculated to second order in $\mathbf{x}$ by applying the ordinary perturbation theory as follows:

$$\begin{aligned} U(\mathbf{x}) &= \epsilon_0(\bar{Q}_{II} + \mathbf{x}) - \epsilon_0(\bar{Q}_{II}) \\ &= v + \mathbf{a}_0 W \mathbf{a}_0 - \sum_{i=1}^2 \frac{(\mathbf{a}_i W \mathbf{a}_0)^2}{\epsilon_i(\bar{Q}_{II}) - \epsilon_0(\bar{Q}_{II})}, \end{aligned}$$

where v is $(\beta/2)(x_\epsilon^2 + x_\eta^2 + x_t^2)$; w the matrix that is difference between the matrix W , with $Q_k = \bar{Q}_k + x_k$ and the one, with $Q_k = \bar{Q}_k$. The summation of the last term is taken over two excited states (2.17a, b). A straightforward calculation leads to

$$\begin{aligned} U(\mathbf{x}) &= \left[\frac{1}{2}\beta + \frac{1}{8}(B - 3K_1 - 3K_2) \right. \\ &\quad \left. - \frac{1}{6} \frac{(3\beta - 2B - 3B' - 6K_1 - 3K_3)^2}{3\beta + B - 3K_1 - 3K_2} \right] \\ &\quad \times (x_\epsilon^2 + x_\eta^2) + [\frac{1}{2}\beta - \frac{1}{4}B - K_1]x_t^2 \\ &\quad + \left[-B' - K_3 \right. \\ &\quad \left. + \frac{(3\beta - 2B - 3B' - 6K_1 - 3K_3)^2}{3(3\beta + B - 3K_1 - 3K_2)} \right] x_\epsilon x_\eta, \end{aligned}$$

where we omit terms linear in $\mathbf{x}$ since these terms must be vanishing at the extremal point $\bar{Q}_{II}$. The conditions for the energy increment $U(\mathbf{x})$ to be positive for arbitrary increment $\mathbf{x}$ are

$$B' < \frac{1}{4}B + \beta - K_1 - K_2 - K_3, \quad (3.4a)$$

$$\begin{aligned} &\beta + \frac{1}{4}B - (K_1 + K_2) \\ &\quad - \frac{2}{3} \frac{(3\beta - 2B - 3B' - 6K_1 - 3K_3)^2}{B + 3(\beta - K_1 - K_2)} \\ &\quad + B' + K_3 > 0, \end{aligned} \quad (3.4b)$$

and $B < (3\beta/2) - 3K_1$, which is identical with (3.2b).

We now plot the region where these inequalities are satisfied on a graph with the x and y axes labeled by B/β and B'/β , respectively. The graph is shown in Fig. 1, where the region of orthorhombic stability is illustrated by the shaded area. The four straight lines (i), (ii), (iii) and (iv) represent (3.1), (3.2b), (3.3) and (3.4a), respectively. It is easily shown that the region determined by these inequalities also satisfies the inequality (3.4b).

We will discuss in detail the effects of the quadratic terms in four cases (T_1, A_2) , (T_1, E) , (T_1, T_1) and (T_1, T_2) . One can obtain a graph characteristic to each of the four cases, substituting into K_1 , K_2 and K_3 the explicit expressions given in Table 1. It is, however, to be noted that the four lines have characteristic features common for the four cases. The line (i) has negative inclination; the line (iv)

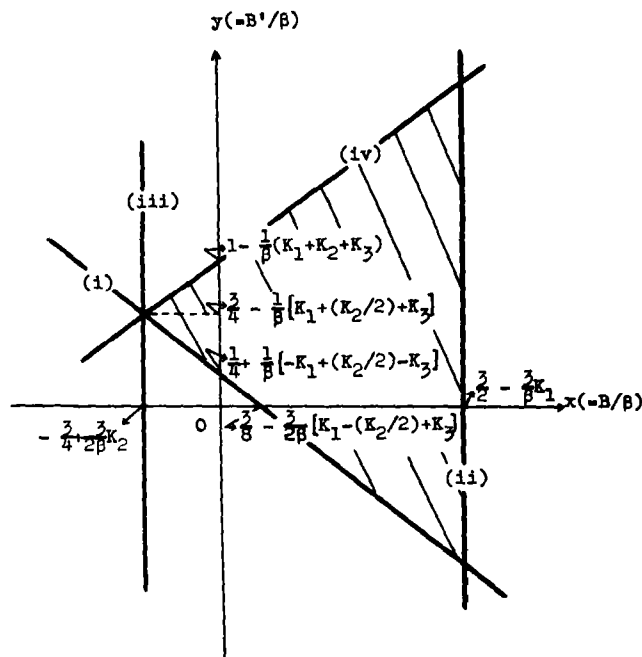


Fig. 1. The region where the conditions (A) and (B) are satisfied is shown by the shaded area in the x - y plane. Four straight lines (i), (ii), (iii) and (iv) represent the inequalities (3.1), (3.2b), (3.3) and (3.4a), respectively.

positive one. Two lines, (ii) and (iii), are parallel to the y axis.

In the cases (T_1, A_2) and (T_1, E) , the straight line (i) intersects the y axis at a point of positive value; and the straight line (ii) the x axis at the point $x = 3/2$. If the straight line (iii) comes to on the right side of the line (ii) beyond $x = 3/2$, we have no longer the shaded region. This fact restricts the values of C_i^2/δ_i ($i = 1$ or 2) which are compatible with the orthorhombic distortion; the values are found to be between zero and $3\beta/2$ for the cases where $B \neq 0$ and $B' \neq 0$ or $B \neq 0$ and $B' = 0$. If $B = 0$ and $B' \neq 0$, the region, $\beta/2 < (C_i^2/\delta_i) < 3\beta/2$, is excluded from the region, $0 < (C_i^2/\delta_i) < 3\beta/2$, since the line (iii) is on the left side of the y axis in this case. Furthermore, if the quadratic interaction $H_e^{(2)}$ is completely neglected, i.e., $B = B' = 0$, the orthorhombic distortion can never be stable.

In the case (T_1, T_1) , a straight line (iii) intersects the x axis at the point $x = -3/4$; the line (iv) the y axis at the point $y = 1$; and the line (i) the x axis at the point $x = 3/8$ and the y axis at the point $y = 1/4$. Only the straight line (ii) varies with a value of C_3^2/δ_3 . The orthorhombic distortion can be stable when the line (ii) intersects the x axis at a point of value larger than $x = -3/4$. Then the values of C_3^2/δ_3 stabilizing orthorhombic distortion are lying in the region $0 < C_3^2/\delta_3 < 3\beta/4$. This is valid for $B \neq 0$ and $B' \neq 0$. If $B = 0$ and $B' \neq 0$, the region, $\beta/2 < C_3^2/\delta_3 < 3\beta/4$, is excluded from the above region; if $B \neq 0$ and $B' = 0$, the region $3\beta/8 < C_3^2/\delta_3 < 3\beta/4$, is excluded. The condition for this exclusion is determined by the position of the straight line (ii).

In the case (T_1, T_2) , the straight lines (ii) and (iii) reduce to $x = (3/2) - (3C_4^2/\beta\delta_4)$ and

$x = -3/4$, respectively; the lines (i) and (iv) intersect the y axis at the points of values $y = (1/4) - (2C_4^2/\beta\delta_4)$ and $y = 1 - (2C_4^2/\beta\delta_4)$, respectively. The values of C_4^2/δ_4 stabilizing the orthorhombic distortion are restricted in the region $0 < C_4^2/\delta_4 < 3\beta/4$. This stabilization always occurs if $B \neq 0$ and $B' \neq 0$. To examine the possibility of orthorhombic distortion for three cases, (a) $B = B' = 0$, (b) $B = 0, B' \neq 0$, (c) $B \neq 0, B' = 0$, let us divide the region $0 < C_4^2/\delta_4 < 3\beta/4$ into three regions, $(0, \beta/8)$, $(\beta/8, \beta/2)$ and $(\beta/2, 3\beta/4)$. In the first region, $0 < C_4^2/\delta_4 < \beta/8$, the shaded region does not contain the origin, $B = B' = 0$, but finite parts of x and y axes. This observation leads us to that orthorhombic distortion does not occur for case (a), but for cases (b) and (c). In the second region, $\beta/8 < C_4^2/\delta_4 < \beta/2$, the shaded region contains the origin, and finite parts of the x and y axes. We note that orthorhombic distortion can occur not only for cases (b) and (c) but even for case (a). The orthorhombic distortion for case (a), $B = B' = 0$, is caused by the inter-level interaction between T_1 and T_2 levels through the linear interaction $H_e^{(1)}$. This result is completely different from the (T_1, A_2) , (T_1, E) and (T_1, T_2) cases. In the third region, $\beta/2 < C_4^2/\delta_4 < 3\beta/4$, the shaded region does not contain the origin and both the x and y axes. Orthorhombic distortion therefore can not occur for cases (a), (b) and (c).

4. CONCLUSION

We have investigated the effects of the

quadratic terms of vibronic interactions in some detail for a particular case where linear and quadratic effects associated only with T_2 mode are considered. It is assumed that the spacing of the electronic levels is so large compared with the vibronic interactions that we may use the ordinary perturbation theory rather than the procedure proposed by Stoneham and Lannoo[5]. We have found that introducing the quadratic terms can lead to the orthorhombic Jahn-Teller distortion of an octahedral complex.

It may be possible that the low symmetry distortion discussed above interprets the electron paramagnetic resonance data for S^- ion in some alkali halides [6].

Acknowledgement—The authors express their hearty thanks to Professor H. Watanabe for his encouragement and many useful discussions.

REFERENCES

1. JAHN H. A. and TELLER E., *Proc. R. Soc. A* **161**, 220 (1937).
2. STURGE M. D., *Solid State Physics* (Edited by F. Seitz and D. Turnbull), Vol. 20, p. 92. Academic Press, New York (1962).
3. HAM F. S., *Jahn-Teller Effects on Electron Paramagnetic Resonance Spectra*, Technical Information Series, No. 68-C-246, General Electric Co. (1968).
4. ÖPIK U. and PRYCE M. H. L., *Proc. R. Soc. A* **238**, 425 (1957).
5. WYSLING P. and MÜLLER K. A., *Phys. Rev.* **173**, 327 (1968).
6. STONEHAM A. M. and LANNOO M., *J. Phys. Chem. Solids* **30**, 1769 (1969).
7. VANNOTTI L. E. and MORTON J. R., *Phys. Rev.* **174**, 448 (1968).

ELECTRO-REFLECTANCE NEAR THE FUNDAMENTAL EDGE OF GaSe

Y. SUZUKI and Y. HAMAKAWA

Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, Japan

and

H. KIMURA, H. KOMIYA and S. IBUKI

The Central Research Laboratories, Mitsubishi Electric Corporation, Amagasaki, Japan

(Received 29 December 1969)

Abstract—Electro-reflectance of GaSe single crystal has been investigated in the spectral region from 1.97 to 2.13 eV. By analyzing the electro-reflectance signals with Kramers-Kronig relation, the energies of the exciton levels and the fundamental edge are assigned both at 300 and 90°K. An additional new structure is observed below the ground state exciton. Electric field and temperature dependences of the structure have been explored and a possibility of the existence of some local states (defect or impurity state) is postulated and discussed.

1. INTRODUCTION

IN THE recent few years, the investigations on layer structure semiconductors have been successfully developed in both theoretical [1-3] and experimental [4-7] point of views, because two dimensional crystals have many interesting properties based upon their special electronic band structures, such as anisotropic conduction and anisotropy of optical constants. Among this type of semiconductors, GaSe has been intensively investigated from measurements of the electrical and optical properties, and also on an aspect of the band structure calculations.

Electro-optical studies combined with modulation techniques [8-10] have recently become a useful tool for the investigation of band structure of solids. The electro-optical measurement has many advantages like better resolution for resolving the band edge energy than present available method. However, there has been no experimental work on the electro-optical effects in the layer semiconductors. This paper presents an experimental result on the electro-reflectance effects near the fundamental edge of GaSe. The measurements were performed in the temperature region from 300 to 90°K. The energies of the exciton states and the

fundamental edge are assigned at each temperature measured. An anomalous structure having extraordinarily field sensitive in amplitude is observed and a possible explanation is made by assuming the presence of a local state in the forbidden band.

2. MEASUREMENT TECHNIQUE

Electro-reflectance measurement was carried out by modulating a field in the interface barrier potential of the GaSe-SnO₂ hetero-junction. The flat band modulation technique [11] were employed by using square wave pulses having a repetition rate of 200 c/s. The incident light was also modulated sinusoidally by the piezo-Bimorph in 90 c/s. The electronic and optical systems for the simultaneous detection of $\Delta R(E)$ and $R(O)$ used in this study were similar to those of our previous work [12, 13]. The resolution of the optical system was about 1 meV. Impurity undoped GaSe single crystal was grown by a Bridgman method [15]. Most of the crystals used as the samples were *p*-type having the resistivity of about 10 Ω -cm. An ohmic contact to GaSe was obtained by painting In-Hg amalgam on the cleaved *c*-plane of GaSe and successive heat treatment in

N_2 gas atmosphere. Growth of the transparent tin oxide on the GaSe and making a hetero-junction were performed by evaporation of pure tin on a cleaved *c*-plane of GaSe single crystal and subsequent thermal oxidation. The SnO_2 layers grown by this technique were almost transparent for photon energies up to 3.1 eV and they have no special absorption structures in this spectral region.

3. EXPERIMENTAL RESULTS

Figure 1 shows the electro-reflectance spectra near the fundamental edge measured with three different electric fields at 300°K. The results of similar measurements at 90°K

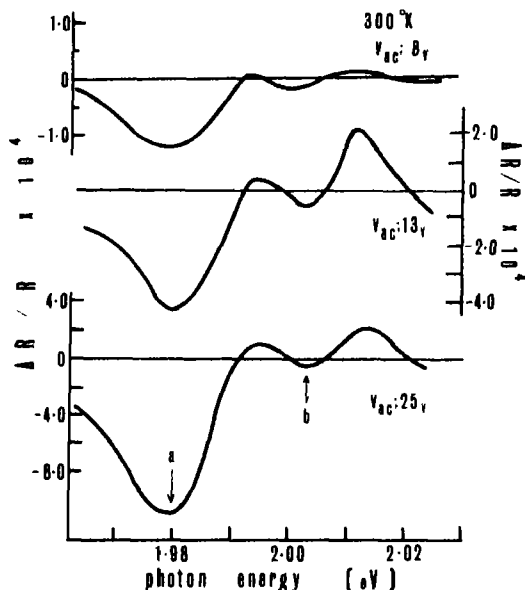


Fig. 1. Electro-reflectance spectra near the fundamental edge of GaSe measured at 300°K with three different electric fields.

also shown in Fig. 2. As can be seen in these figures, a significant variations of the line structure with electric field are observed particularly at low temperatures, that is; the amplitude of these structures increase with increasing applied voltage, and at low temperature the magnitudes are much larger than

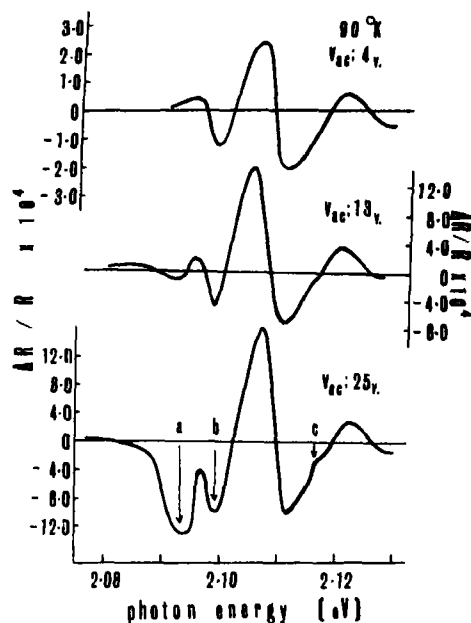


Fig. 2. A variation of electro-reflectance spectra with electric field near the fundamental edge measured at 90°K.

those at room temperature with same bias voltages. Moreover, in the higher applied voltage at low temperature it is seen that new structure *c* appears. To clarify the source of these complicated variations of the line shape, these $\Delta R/R$ spectra are transformed into the field induced change in the imaginary part of dielectric constant, $\Delta\epsilon_2$, through Kramers-Kronig relation. In the process of the *K-K* transformation, it is assumed that the extinction coefficient *k* is neglected as compared with the refractive index *n* and that *n* has no spectral variations near the fundamental edge of GaSe similar to the most of semiconductors. A typical calculated result of $\Delta\epsilon_2$ spectrum is shown in Fig. 3. In the figure, the dashed line is $\Delta R/R$ measured at 90°K with the applied voltage 25 V and the solid line shows the $\Delta\epsilon_2$ spectrum transformed from the $\Delta R/R$.

From the detailed observations on the line shapes and their variations with electric

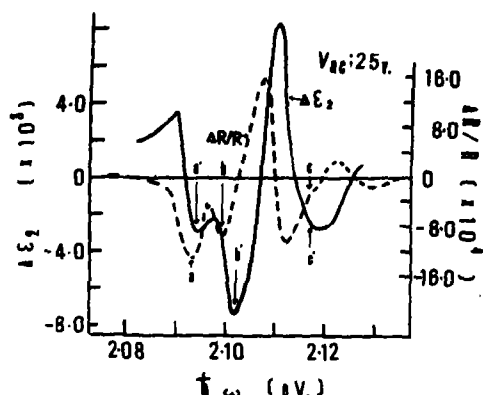


Fig. 3. An imaginary part of the dielectric constant $\Delta\epsilon_2$ spectrum at 90°K transformed from $\Delta R/R$ through Kramers-Kronig relation (solid line) and electroreflectance spectrum $\Delta R/R$ measured at 90°K (dashed line).

field, at least three structures related to the transition level or edge; whose energy positions are relatively insensitive to the electric field; are found as denoted by a, b, c , in Fig. 2. It is noticed that the structure a in Fig. 1 and Fig. 2 has greater field dependence in the amplitude than those of other structures, while the faint structure c observed at 90°K could not be observed at 300°K. As shown in Fig. 4, the structure a and a' , b and b' have respectively the nearly same voltage dependence in the amplitude. The structures notified as a' and b' in the $\Delta\epsilon_2$ spectrum are those

having same sources correspondingly with a and b in the $\Delta R/R$.

4. DISCUSSION

As described in the last section, the energy position of the structure a and b are almost independent of the applied voltage. However the applied voltage dependence on the amplitude of the structure a is much greater than that of the structure b in both temperatures. At 90°K, the amplitude of b is relatively large as compared with that at 300°K, but this relationship is inverted on the structure a . These systematic variations of the amplitude against temperatures and electric fields imply that the sources of the structure a and b should be different kind of transition levels (or edge).

Kamimura and Nakao[1] have demonstrated from the band structure calculation that the fundamental edge has three dimensional M_0 type band edge and the optical transition is allowed one, when the electric field vector of the incident light is perpendicular to c -axis. The samples and optical system employed in the present experiment are arranged in this alignment. Since the exciton ground state has been already observed around energy of 2.10 eV at 77°K and also from the fact that the fundamental edge in GaSe is determined to be 2.12 eV at 77°K[15], it is

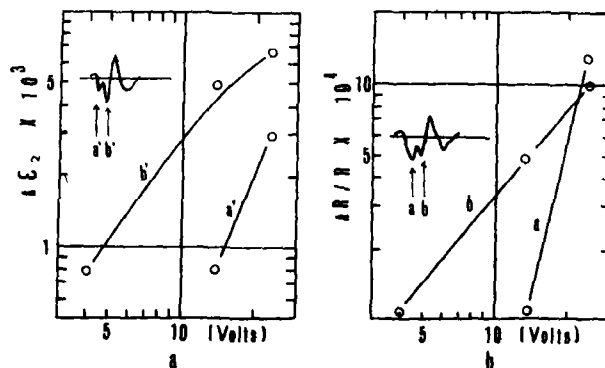


Fig. 4. The applied voltage dependence on the amplitude of the structure a' and b' in $\Delta\epsilon_2$ (a), a and b in $\Delta R/R$ (b) at 90°K.

thought that the structure a' or b' must be correlated to the exciton. The largest difference between a' and b' exists in their temperature dependence, that is, the amplitude of b' decreases with increasing temperature, while that of a' behaves inversely. Hamakawa *et al.*[16] have experimentally shown the thermal broadening of exciton on the electro-absorption. Recently Snabely *et al.*[17] and Gutche and his co-workers[18] have independently observed a strong temperature dependence of the differential absorption coefficient; $\Delta\alpha$ in the exciton lines of CdS. A theoretical treatment on the excitonic effect in the electro-optical studies has been given by Duke, Alferieff[19] and quite recently by Enderlein[20]. According to their results, the exciton absorption line is broadened by an electric field and its peak shifts to the higher energy side. Figure 5 shows a schematic representation of the

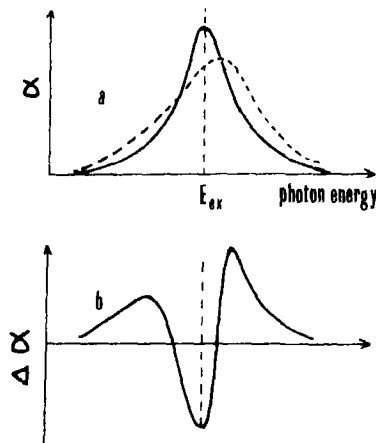


Fig. 5. (a) Schematic representation of the effect of electric field on the excitonic absorption; the solid line expresses the line with zero field and the dashed line with field. (b) The field induced change in the excitonic absorption $\Delta\alpha(E)$.

effect of electric field on the excitonic absorption line. Considering Lorentzian type thermal broadening, the exciton line without field is drawn by solid line in the Fig. (a) and the line with field is shown by dashed line. Thus

an apparent change in the differential absorption coefficient $\Delta\alpha$ might have a structure as shown in the Fig. (b). As seen in this figure, the negative peak in $\Delta\alpha$ corresponds to the exciton level. These evidences indicate that the structure b' observed might be associated with the exciton ground state of GaSe whose energy level is estimated to be 2.102 eV at 90°K and 2.003 eV at 300°K.

Regarding the structure c , there is no clear identification at the present stage of experiment. However, from the energy location relative to the exciton ground state assigned here, the structure might be associated with either the fundamental edge or the exciton second state. It will be generally expected, in the wide gap semiconductors having relatively small exciton binding energy, that no clear fundamental absorption edge isolated from the exciton has been observed both in static absorption and electro-optical experiment, because of an overlapping of broadened signals due to the thermal broadening. The energy separation between b' and c' is estimated to be 17 meV at 90°K. According to Mooser *et al.*[5,15] the exciton binding energy of GaSe has been already reported to be 20 meV. Using this value and assuming the Wannier type exciton, the energy separation between the exciton ground and second state is calculated to be 15 meV. This value nearly coincides with the observed energy separation between b' and c' in Fig. 3. Following this argument, location of the fundamental edge can be calculated as 2.030 eV at 300°K and 2.124 eV at 90°K. These values are consistent with those obtained by other experiments[5,15,23]. Further experimental evidence on the structure c' at low temperature (Liq. He. temperature) and more clear identification will be given in the future.

The temperature and applied voltage dependence of the structure a behaves quite different from those of the electroreflectance signals of the exciton discussed above. This large dependence on the electric fields

resembles to that of the structure originated from an impurity level as already reported in GaAs²¹. Since SnO₂-GaSe hetero-junction are prepared by oxidization of Sn-GaSe, it is possible to contain some defects or impurities at the interface of SnO₂-GaSe hetero-junction. Thus, it is proposed that the structure *a'* might be due to an impurity or defect state. The tendency of the temperature dependence of the amplitude in the structure *a* also

even in taking into account the temperature dependence of the energy gap. We have tried to calculate the temperature coefficient of energy gap; β_{Eg} and that of the localized level; β_l from our data, and obtained the values of $\beta_{Eg} = 4.52 \times 10^{-4}$ and $\beta_l = 5.09 \times 10^{-4}$ (eV/°K). Seraphin have also found relatively large β_l in GaAs and reported the value of 6×10^{-4} eV/°K.

In conclusion, the values of energy levels

Table 1. A comparison of the structure energies assigned by previous works and present measurement

Source (Authors)	Temperature	E_{ex1}	E_{ex2}	E_g	Binding energy of exciton B
	(°K)	(eV)	(eV)	(eV)	(meV)
Optical absorption (Bassani <i>et al.</i> [22])	300	2.003			
Electro-reflectance Present work	300	2.007		2.030	23
Optical absorption (Bassani <i>et al.</i> [22])	78	2.102	2.130	2.139	37
Optical absorption (Mooser <i>et al.</i> [15])	77			2.120	20
Electro-reflectance Present work	90	2.101	2.118	2.124	23
Magneto-optical effect (Aoyagi <i>et al.</i> [6])	4.2			2.132	10
Magneto-absorption (Halpern [23])	4.2	2.109		2.130	20
Optical absorption (Mooser <i>et al.</i> [5])	4.2	2.1095	2.1244		
Theoretical (Kamimura, Nakao [1])					27

supports this argument. The energy of this state is estimated to be 1.986 eV at 300°K and 2.093 eV at 90°K. Therefore, the activation energies at both temperatures are 44 meV and 31 meV, respectively. The discrepancy of these two values seems to be a little large,

and states assigned by the present work are summarized together with the values obtained by other workers in Table 1. Figure 6(a) shows the $\Delta\epsilon_2$ spectrum transformed from the electro-reflectance spectrum measured at 90°K, and (b) is a possible structures analyzed

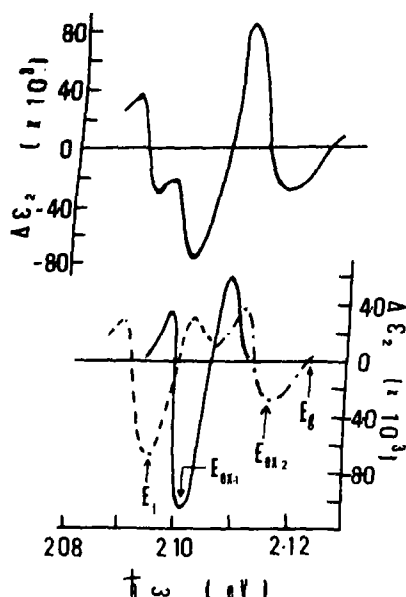


Fig. 6. $\Delta\epsilon_2$ spectrum (a) and possible analyzed signals (b) expected from an impurity state (E_i), the ground state exciton (E_{ex1}) and the fundamental edge with the second state exciton.

from (a). In the figure, the location of each of overlapped structure E_i , E_{ex1} , E_{ex2} and E_u are denoted by their symbols.

REFERENCES

1. KAMIMURA H. and NAKAO K., *J. phys. Soc. Japan Suppl.* **21** 27 (1966); *J. phys. Soc. Japan* **24** 1313 (1968).
2. BASSANI F. and PARRAVICINI G. P., *Nuovo Cim.* **B50**, 95 (1968).
3. FIVAZ R., *J. Phys. Chem. Solids* **28**, 8393 (1967).
4. KAMIMURA H., NAKAO K. and NISHINA Y., *Phys. Rev. Lett.* **22**, 1379 (1967).
5. BREBNER J. L. and MOOSER E., *Phys. Lett.* **24A**, 274 (1967).
6. AOYAGI K., MISU A., KUWABARA G., NISHINA Y., KURITA S., FUKUROI T., AKIMOTO O., HASEGAWA H., SHINADA M. and SUGANO S., *J. phys. Soc. Japan Suppl.* **21**, 174 (1966).
7. BREBNER J. L., FISCHER G. and MOOSER E., *J. Phys. Chem. Solids* **23**, 1417 (1962).
8. FROVA A., HANDLER P., GERMANO F. A. and ASPNES D., *Phys. Rev.* **145**, 575 (1966).
9. SERAPHIN B. O. and BOTTKA N., *Phys. Rev.* **145**, 628 (1966).
10. CARDONA M., SHAKLEE K. and POLLACK F. H., *Phys. Rev.* **154**, 696 (1967).
11. HAMAKAWA Y., GERMANO F. A. and HANDLER P., *Phys. Rev.* **167**, 703 (1968).
12. HAMAKAWA Y., NISHINO T. and YAMAGUCHI J., *Proc. Int. Conf. Phys. Semiconductors*, p. 385 (1968).
13. IKEDA K., HAMAKAWA Y., KOMIYA H. and IBUKI S., *Phys. Lett.* **28A**, 647 (1969).
14. BUBE R. H. and LINDE E. L., *Phys. Rev.* **115**, 1159 (1959).
15. AULICH E., BREBNER J. L. and MOOSER E., *Phys. Status Solidi* **31**, 129 (1969).
16. HAMAKAWA Y., GERMANO F. A. and HANDLER P., *Proc. Int. Conf. Phys. Semiconductors, Kyoto J. phys. Soc. Japan Suppl.* **21**, 111 (1966).
17. SNABELY B., *Solid St. Commun.* **14**, 561 (1966).
18. GUTCHE E. and LANGE H., *Phys. Status Solidi* **32**, 293 (1969).
19. DUKE C. B. and ALFERIEFF M. E., *Phys. Rev.* **145**, 583 (1966).
20. ENDERLEIN R., *Phys. Status Solidi* **26**, 509 (1968).
21. SERAPHIN B. O., *J. appl. Phys.* **47**, 721 (1966).
22. BASSANI F., GREENAWAY D. L. and FISCHER G., *Proc. Int. Conf. Phys. Semiconductors, Paris*, p. 51 (1964).
23. HALPERN J., *Proc. Int. Conf. Phys. Semiconductors, Kyoto* (1966). *J. phys. Soc. Japan* **21**, Suppl. 180 (1966).

ASYMMETRIC NUCLEAR MAGNETIC RESONANCE LINE SHAPES DUE TO NUCLEAR QUADRUPOLE AND ANISOTROPIC SHIFT INTERACTIONS*

P. W. FRANCE† and H. O. HOOPER

Department of Physics, Wayne State University, Detroit, Mich. 48202, U.S.A.

(Received 10 September 1969; in revised form 22 December 1969)

Abstract—The symmetry of the central component of a polycrystalline NMR line shape caused by nuclear quadrupole and anisotropic magnetic interactions has been examined theoretically. The asymmetry of the line shape is measured as the difference in the distances from the peaks of the first derivative to the center of the line. This asymmetry is found to vary as the square of the quadrupole coupling constant and inversely as the NMR frequency for the quadrupole interaction. For the anisotropic magnetic interaction the asymmetry varies as the cube of the frequency. The results of the calculations are discussed with respect to conditions and applications.

1. INTRODUCTION

THE EXTRACTION of the nuclear quadrupole coupling constant, asymmetry parameter η , and anisotropic magnetic shift $K_{||}$ from nuclear magnetic resonance (NMR) spectra is of particular importance in determining the internal electric and magnetic fields and the atomic bonding in a given material. If single crystals of a material are not available or are not experimentally feasible as in the case of metallic conductors and amorphous materials, all values of interest must be obtained using a polycrystalline sample. Then the NMR line shape is the sum of the contributions from each nucleus randomly oriented in the sample. The calculation of the NMR line shape from polycrystalline samples due to first-order quadrupole splitting with any asymmetry is given in a review article by Cohen and Reif [1]. The second order shape is also given but only for the case of axial symmetry. For non-axial symmetry several authors have obtained results [2, 3] with the most complete examination given by Marita, Umeda, and Kusumoto [4].

The line shape due to anisotropic magnetic shifts of any asymmetry have been treated by Bloembergen and Rowland [5]. Consideration of both of the above interactions on the line shape is dealt with by Jones, Graham, and Barnes [6].

In most of the previous work, because of the prohibitive complexity involved, the method employed is that of computing the line shape assuming no line broadening and adding small broadening as a smoothing process later. A few authors [2, 4] have used computerized methods for adding distinct values of broadening. This work, however, is concerned with the opposite case in which the line broadening is assumed large so that the line shape is that of one large asymmetric line (Fig. 1). The purpose is then to relate the asymmetry of the resonance line to the quadrupole coupling constant, η , and $K_{||}$.

(a) *Quadrupole effect*

If a nucleus of spin I which has a quadrupole moment is placed in a magnetic field, its energy level is split into $2I + 1$ levels. For a nonzero electric field gradient the magnetic resonance line is split into $2I$ components. A half integer nuclear spin spectrum has a central component corresponding to the

*Work supported in part by U.S. Atomic Energy Commission.

†Present address: Department of Physics, University of Louisville, Louisville, Kentucky 40208, U.S.A.

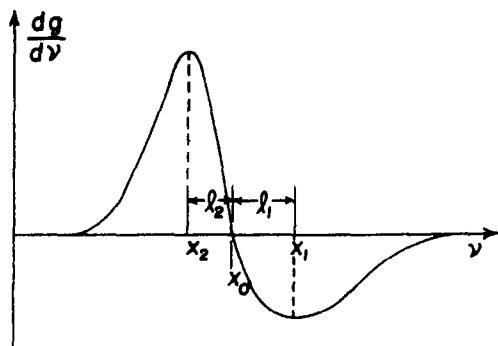


Fig. 1. First derivative of an asymmetric line shape.

$m = \frac{1}{2} \leftrightarrow m = -\frac{1}{2}$ transition which is undeviated by a quadrupole interaction in first order perturbation theory. Expressed in a coordinate system in which the electric field gradient is diagonal, second order perturbation shifts this line by the amount [4]

$$\nu_{1/2}^{(2)} = Df(\mu\phi) \quad (1)$$

where

$$D = -(\nu_Q^2/6\nu_L)(a - \frac{3}{4}),$$

$$f(\mu\phi) = A(\phi)\mu^4 + B(\phi)\mu^2 + C(\phi),$$

$$\mu = \cos \theta,$$

$$A(\phi) = -\frac{27}{8} - \left(\frac{9}{4}\right)\eta \cos 2\phi - \left(\frac{3}{8}\right)\eta^2 \cos^2 2\phi,$$

$$B(\phi) = \frac{30}{8} - \left(\frac{1}{2}\right)\eta^2 + 2\eta \cos 2\phi + \left(\frac{3}{4}\right)\eta^2 \cos^2 2\phi,$$

$$C(\phi) = -\frac{3}{8} + \left(\frac{1}{3}\right)\eta^2 + \left(\frac{\eta}{4}\right)\cos 2\phi - \left(\frac{3}{8}\right)\eta^2 \cos^2 2\phi,$$

$$\nu_Q = 3e^2qQ/2I(2I-1)h,$$

$$\nu_L = g\beta H/h,$$

$$a = I(I+1),$$

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}}, \quad 0 < \eta < 1$$

$$eq = V_{zz}.$$

The Eulerian angles θ , ϕ , and ψ are as defined in Ref. [4], where they specify the orientation between the frame in which the Zeeman energy is diagonal and the frame in which the electric field gradient is diagonal.

The line shape $g(x)$ from a polycrystalline sample then will be the sum of the lines from each crystal orientation given in equation (1). Hence

$$g(x) = \alpha \int_0^{2\pi} \int_{-1}^1 S d\mu d\phi, \quad (2)$$

where $x = \nu - \nu_L$, integration is over the whole solid angle Ω , and α is a constant. The quantity S is a function of $x - Df(\mu\phi)$ and is merely the average line shape of each individual line. The x expresses a shift of the zero point of the line from ν_L . Use has been made of the fact that there is a random angular distribution of nuclei. It will be assumed that the individual lines are of the form

$$S = \exp[-2\lambda(x - Df)^2/\sigma^2]. \quad (3)$$

Here σ is readily identified as the peak-to-peak width of the first derivative. The parameter λ is used for expanding the exponential and is numerically equal to one.

For a symmetric line the peaks of the first derivative will lie an equal distance on both sides from the center at ν_L . One of the ways the asymmetry manifests itself is that these distances become unequal and, as shall be shown, the center of the line shifts. The procedure shall then be to take the first and second derivatives of $g(x)$, set them equal to zero, and solve for x . This will give the center of the line, as defined by a zero crossing point and the position of the first derivative peaks.

Substitution of equation (3) into equation (2) and differentiating gives

$$g'(x) = -(4\lambda/\sigma^2)\{xg(x) - \alpha D \times \int f \exp[-2\lambda(x - Df)^2/\sigma^2] d\Omega\}, \quad (4)$$

$$g''(x) = -(4\lambda/\sigma^4)\{\sigma^2g(x) - 4x^2\lambda g(x)\}$$

$$+ 8\alpha\lambda D x \int f \exp[-2\lambda(x - Df)^2/\sigma^2] \\ \times d\Omega - 4\alpha\lambda D^2 \int f^2 \\ \times \exp[-2\lambda(x - Df)^2/\sigma^2] d\Omega\}. \quad (5)$$

Setting $g'(x) = 0$ and expanding* the remaining exponentials in a series in powers of λ gives after integration

$$x[4\pi + (4xDa_1 - 2D^2a_2)\lambda/\sigma^2 + (16x^2D^2a_2 \\ - 8xD^3a_3 + 4D^4a_4)\lambda^2/\sigma^4 + (64x^3D^3a_3 \\ - 96x^2D^4a_4 + 48xD^5a_5 - 8D^6a_6)\lambda^3/\sigma^6 + \dots] \\ - D[a_1 + (4xDa_2 - 2D^2a_3)\lambda/\sigma^2 + (16x^2D^2a_3 \\ - 8xD^3a_4 + 4D^4a_5)\lambda^2/\sigma^4 + (64x^3D^3a_4 \\ - 96x^2D^4a_5 + 48xD^5a_6 - 8D^6a_7)\lambda^3/\sigma^6 + \dots] \\ = 0 \quad (6)$$

where

$$a_n(\eta) = \int f^n(\mu\phi) d\Omega.$$

This work is concerned with the case in which the external broadening is large, so that the line shape is that of one large asymmetric line (Fig. 1). This corresponds to the condition that $D^2/\sigma^2 \ll 1$. If terms of the same power of x are collected together and λ set equal to one, then equation (6) can be reduced to equation (7) using the condition $D^2/\sigma^2 \ll 1$.

$$-Da_1/\sigma + 4\pi x/\sigma + 4Da_1x^2/\sigma^3 \\ + 16D^2a_2x^3/\sigma^5 + \dots = 0. \quad (7)$$

Now the point of zero slope of an absorption curve, the first derivative of which is illustrated in Fig. 1, must be expressed by an equation which is at least linear in x . Quadratic and higher order equations in x can be used with the extraneous roots ignored as

*The absolute value of the n th term in each expansion in equations (4) and (5) can be shown to be less than $b|4xD - 2D^2|^{n-1}/(n-1)!$ whose sum from $n=1$ to $n=\infty$ is $b \exp|4xD - 2D^2|$, and where $b > 4\pi$. Then by the comparison test each expansion is convergent.

being non-physical, but notice in equation (7) that the coefficients of the x^2 and x^3 terms are much smaller than the coefficients of the x term by the condition that $D/\sigma \ll 1$. Terminating equation (7) after that power of x which has the largest coefficient gives a linear equation which when solved for x gives the center of the line at

$$x_0 = Da_1/4\pi. \quad (8)$$

Using the same procedure for $g''(x)$, simplifying the integrals, expanding the remaining exponentials, integrating, setting λ equal to one, using the condition $D/\sigma \ll 1$ and finally collecting terms of the same power of x gives for $g''(x) = 0$ the equation

$$4\pi + 12Da_1x/\sigma^2 - 16\pi x^2/\sigma^2 - 16Da_1x^3/\sigma^4 \\ + \dots = 0. \quad (9)$$

Since there are only two points of zero slope in the first derivative curve of Fig. 1, equation (9) must be terminated so that it is at least quadratic in x . Since the x^3 and the higher order terms are negligible, the solutions to equation (9) are

$$x_1 = \sigma'/2 + 3Da_1/8\pi, \\ x_2 = -\sigma'/2 + 3Da_1/8\pi, \quad (10)$$

where

$$\sigma' = \sigma[1 + 9D^2a_1^2/16\pi^2\sigma^2]^{1/2} \approx \sigma \\ \text{for } D^2/\sigma^2 \ll 1.$$

It can be seen from Fig. 1 that the new peak-to-peak width of the derivative curve is just $x_1 - x_2 = \sigma'$.

Now if the difference $\Delta l = l_2 - l_1$ (Fig. 1) is taken as our measure of asymmetry then

$$\Delta l = -Da_1/4\pi = (\nu_0^2/30\nu_L)(a - \frac{1}{2})(1 + \eta^2/3). \quad (11)$$

To determine equation (11) data from Table 1 were employed. From equation (11) it is

Table 1. Interaction coefficients

a_i^*	Quadrupole interaction	Anisotropic magnetic interaction
a_1	$(4\pi/5)(1 + \eta^2/3)$	0
a_2	$72\pi/105$	$4\pi/5$
a_3	0.302π	$8\pi/5$
a_4	0.207π	0.343π
a_5	0.115π	0.208π
a_6		0.212π
a_7		0.017π

*Only a_1 has been calculated for $\eta \neq 0$

apparent that the amount of asymmetry is proportional to the square of the quadrupole coupling constant and inversely proportional to ν_L , as might be expected from purely physical reasoning.

The terms that are neglected have been assumed small in comparison with those that are kept. This will of course depend on the value of D^2/σ^2 , which has been assumed $\ll 1$. If D^2/σ^2 becomes too large then the absorption curve will take a shape similar to those considered elsewhere [1-4, 6]. The above terminations would then not be adequate since cubic, biquadratic and higher order equations in x would be needed to account for the increasing number of points of zero slope.

A computer evaluation for the same conditions for the peak-to-peak line width has been published by Casabella [2]. This allows a comparison to be made for those values where $D/\sigma \ll 1$. It should be mentioned to eliminate confusion that Casabella's definition of σ is equal to $\frac{1}{2}$ of our definition of σ . His results have been changed to fit our definition. $\delta\nu_2$ is defined as the peak-to-peak width of the polycrystalline line which in this paper has been denoted by σ' , and σ is the peak-to-peak width of the Gaussian single crystal line. From equation (10) $\delta\nu_2/\sigma = \sigma'/\sigma \approx 1$ for $D^2/\sigma^2 \ll 1$. From Casabella's work for D^2/σ^2 equal to 1/56, 1/36 and 1/3.5, $\delta\nu_2/\sigma$ is equal to 1.005, 1.010 and 1.095 respectively which agrees very well with our result that $\sigma'/\sigma \approx 1$.

(b) Anisotropic magnetic shift effect

It has been shown that the second-order contribution of the anisotropic magnetic shift is negligibly small [6]. Therefore, it is only necessary to calculate the first order contribution. Following the discussion of Abragam [7], the Zeeman frequency in the principal axis system of the anisotropic shift tensor for axial symmetry is

$$\nu(\mu\phi) = \nu_L(1 + K) + Df(\mu) \quad (12)$$

where

$$D = \nu_L K_{\parallel},$$

$$f(\mu) = (3\mu^2 - 1)/2, \quad \mu = \cos \theta,$$

and K and $K_{\parallel}$ are the isotropic and anisotropic shifts respectively. If $x = \nu - \nu_L(1 + K)$ then the line shape function will take on the same form as equation (2) and equation (3) using the above D and f . Thus $g'(x)$ and $g''(x)$ will be equations (4) and (5) respectively. However, as can be seen from Table 1, a_1 is now zero. This means that equations (7) and (9) will have different coefficients from those for the quadrupole interaction, when the condition $D^2/\sigma^2 \ll 1$ is applied. If the equations for $g'(x)$ and $g''(x)$ are set equal to zero, then the center of the absorption curve, x_0 , and the two solutions corresponding to points of zero slope of the derivative curve are found to be

$$x_0 = -D^3 a_3 / 2\pi\sigma^2, \quad (13)$$

$$x = -5D^3 a_3 / 4\pi\sigma^2 \pm \sigma' / 2 \quad (14)$$

where

$$\sigma' = \sigma [1 + 25D^6 a_3^2 / 4\pi^2 \sigma^6]^{1/2} \approx \sigma \quad (15)$$

$$\text{for } D^2/\sigma^2 \ll 1.$$

It can be seen from equation (14) that σ' is again the peak-to-peak width of the first derivative curve.

The line asymmetry using equations (13)

and (14) now becomes

$$\Delta l = l_2 - l_1 = 3D^3a_3/2\pi\sigma^2. \quad (16)$$

Thus the line asymmetry in terms of the anisotropic constants is

$$\Delta l = 12(\nu_L K_{||})^3/35\sigma^2 \quad (17)$$

and $\sigma' = \sigma$.

2. DISCUSSION

It has already been mentioned that the individual lines are assumed to be gaussian in shape and of an average width σ . It should also be noted that σ may be due to any interaction and that σ has been considered independent of angular orientation. It may well be that for very large broadening σ may depend on ν_L , which will alter the dependence of Δl on ν_L in the anisotropic magnetic interaction case. It should also be pointed out that for the quadrupole interaction (equation 10) the asymmetry of the resonance line Δl is independent of σ and is only affected by a non-axial symmetric electric field gradient in $\eta^2/3$. Thus, for an asymmetry parameter of $\eta < 0.5$ the percentage error in the quadrupole coupling constant as determined from a measure of Δl assuming axial symmetry ($\eta = 0$) is $(50/3)\eta^2$. The value of using the measure of Δl in equation (11) to determine the quadrupole coupling constant lies in the fact that NMR lines which are only slightly asymmetric due to a small second order quadrupole perturbation can be analyzed readily from the usually observed derivative curves. With such lines it is not usually possible to determine the quadrupole coupling constant employing the fact that the two infinite peaks in the usual theoretical line shape of the absorption curve are separated [1] by $(25/9)A$ (where $A = [\nu_Q^2/16\nu_L](a - \frac{1}{2})$). It should be noted that equation (10) can be used to determine an approximate value for the separation of these two peaks if the restriction on D/σ is not restricted to $D/\sigma \ll 1$.

The quadrupole coupling constant obtained in this manner for the case of a large quadrupole interaction is about 25 per cent larger than the value determined using $(25/9)A$ as the separation between the derivative peaks. The latter being an approximation which in general yields an experimental coupling constant which is too small since the derivative peaks do not correspond to the infinities in the theoretical powder pattern. This comparison gives some indication that our restrictions on D/σ are conservative and that the analysis presented in this paper may be applied in practice to larger values of D/σ .

The method outlined here is also very useful when more than one interaction is responsible for the broadening and asymmetry of the NMR line. For example if both an anisotropic magnetic interaction and a quadrupole interaction are present and do produce a measureable Δl than the total asymmetry will be characterized by the sum of the Δl 's from each of the interactions. These two interactions can be treated separately, since it has been shown [6] that the second order contribution resulting from the interference terms between the anisotropic magnetic shift and quadrupole interactions vanish. In this event a fitted plot of Δl against frequency will provide for a determination of the desired constants. However, care should be taken to replace ν_L by $\nu_0 = \nu_L(1 + K)$ in the quadrupole expression where K is the isotropic shift and $\nu_L K_{||}$ by $(\nu_0 K_{||})/(1 + K)$ in the anisotropic magnetic expression if K is not sufficiently smaller than one.

The results of this analysis have been applied to determine the strength of both the quadrupole interaction and the anisotropic magnetic interaction in several glassy materials [8] where broad asymmetric NMR lines have been observed. In the case of the amorphous materials the NMR lines do not contain any of the first order satellite transitions presumably due to random variations in quadrupole interaction which produces a broadening of the first order satellite lines.

It should be noted, however, that the presence of first order satellites within the central transition does not alter the asymmetry of the resonance lines. The presence of first order satellites which are symmetric with respect to the ν_L has been examined in connection with the analysis described here and no change in the asymmetry or alterations in the results reported here occur.

The method of analysis reported here has been employed to examine the resonance lines from some powdered crystalline materials [9-11], for example V_2O_5 and NbN. This analysis allows one to separate readily the quadrupole and anisotropic magnetic interactions in V_2O_5 . In addition it appears that this analysis would be of use in extracting information from the asymmetric NMR lines observed in several borides and intermetallic materials [12, 13].

REFERENCES

1. COHEN M. H. and REIF F., *Solid State Physics*, Vol. 5, p. 321. Academic Press, New York (1957).
2. CASABELLA P. A., *J. chem. Phys.* **40**, 149 (1964).
3. SILVER A. H. and BRAY P. J., *J. chem. Phys.* **29**, 984 (1958).
4. NARITA K., UMEDA J. and KUSUMOTO H., *J. chem. Phys.* **44**, 2719 (1966).
5. BLOEMBERGEN N. and ROWLAND T. J., *Acta metall.* **1**, 731 (1953).
6. JONES W. H. JR., GRAHAM T. P. and BARNES R. G., *Phys. Rev.* **132**, 1898 (1963).
7. ABRAGAM A., *The Principles of Nuclear Magnetism*, p. 205. Oxford University Press, London (1961).
8. FRANCE P. W., Ph.D. Thesis Wayne State University, December (1967).
9. RAGLE J. L., *J. chem. Phys.* **35**, 753 (1961).
10. NAGASAWA, H., TAKESHITA S. K. and TOMONO Y., *J. phys. Soc. Japan* **19**, 764 (1964).
11. BENNETT R. A., HOOPER H. O. and ROY U., *J. appl. Phys.* **40**, 2441 (1969).
12. SILVER A. H. and KUSHIDA T., *J. chem. Phys.* **38**, 865 (1963).
13. FROIDEVAUX C. and ROSSIER D., *J. Phys. Chem. Solids* **28**, 119 (1967).

EFFECT OF UNIAXIAL STRESS ON *F*-CENTER HYPERFINE INTERACTIONS*†

C. EDWARD BAILEY‡

Physics Department, Dartmouth College, Hanover, New Hampshire 03755, U.S.A.

(Received 15 December 1969)

Abstract—The ENDOR technique is used to measure the effect of uniaxial stress on the *hfi* of the first shell LiF, KCl and KBr ions, second shell KCl ions and fourth shell KBr ions. It is found that motion of the neighboring ions or an admixture of an envelope wave function of the symmetry of the distortion are not enough to explain the results. The discrepancy can be explained by taking into account ionic core distortions. The use of Seidel's Rule to determine the local compressibility gives results that are about equal to those for the bulk crystal. The local motion around the *F*-center is in the same direction as that in the bulk material although of different magnitude.

1. INTRODUCTION

MANY different studies have been made of the *F*-center in the alkali halides[1]. The understanding of the interaction of the *F*-center with the surrounding lattice can be enhanced by performing stress experiments. While the interpretation of the studies of the shift of the optical absorption band with both hydrostatic[2] and uniaxial pressure[3, 4] must consider both the ground state and the excited state, the ground state can be singled out for study by electron paramagnetic resonance (EPR) and electron–nuclear double resonance (ENDOR). The ENDOR technique allows detailed studies of the hyperfine interaction (*hfi*) to be made. We report here an ENDOR study of the effect of uniaxial stress on the *hfi* of the *F*-center.

2. THEORY

2.1 Unstressed crystals

Neglecting second order terms and quadru-

pole interactions ENDOR transitions for a given nucleus occur at the frequencies, f_{ENDOR} , where

$$hf_{\text{ENDOR}} = g_n \beta_n H \pm \frac{1}{2}(a + B_{xx}h_x^2 + B_{yy}h_y^2 + B_{zz}h_z^2) \quad (1)$$

where g_n is the nuclear g -value, β_n is the nuclear magneton, a is the isotropic *hfi* constant, B_{xx} , B_{yy} , B_{zz} are the components of the anisotropic *hfi* tensor and h_x , h_y , h_z are the direction cosines between the principal axes of the *hfi* and the external magnetic field. When there is axial symmetry (1) can be simplified to

$$hf_{\text{ENDOR}} = g_n \beta_n H \pm [\frac{1}{2}a + \frac{1}{2}b(3 \cos^2 \Theta - 1)] \quad (2)$$

where $b = B_{zz}/2$ and Θ is the angle between the interaction axis (defined as the zz anisotropic *hfi* tensor axis) and the external magnetic field. The isotropic and anisotropic *hfi* constants a and B_{ik} are given[5] by

$$a = (8/3)\pi g_n \beta_n g_e \beta_e |\Psi_F(0)|^2 \quad (3)$$

$$B_{ik} = g_n \beta_n g_e \beta_e \int [(3/r^5)x_i x_k - (1/r^3)\delta_{ik}] \times |\Psi_F(r)|^2 dv \quad (4)$$

*Research supported by a grant from the National Science Foundation. A preliminary report of this work has been given: BAILEY C. E. and DOYLE W. T., *Bull. Am. phys. Soc.* 12, 58 (1967).

†The manuscript, completed while the author held a National Research Council Postdoctoral Research Associateship at the Naval Research Laboratory, is partially based upon a thesis submitted for the Ph.D. degree at Dartmouth College.

‡Present address: Naval research Laboratory, Washington, D.C. 20390, U.S.A.

where $i, k = x, y, z$ and $\Psi_F(0)$ is the F -center wave function evaluated at the nucleus under study.

Following Gourary and Adrian[6, 7] an approximate wave function Ψ_F may be obtained by starting with an envelope function, Φ_F , for the F -center electron and then orthogonalizing Φ_F to the nuclear core wave function Ψ_i . Thus

$$|\Psi_F|^2 = N^2 \left[\left(1 - \left(\sum_i \Psi_i \langle \Psi_i | \Phi_F \rangle \right) / \Phi_F \right)^2 \right. \\ \left. \times |\Phi_F|^2 = A |\Phi_F|^2 \right] \quad (5)$$

where N is a normalization factor and A is the amplification factor which depends upon the orthogonalization of the envelope function to the nuclear core functions. A convenient set of wave functions to use for the envelope wave functions are the hydrogen type

$$u_{100} = (Z/R)^{3/2} (\exp(-Zr/R)) / (\pi)^{1/2} \quad (6)$$

$$u_{320} = r^2 (Z'/R)^{7/2} (\exp(-Z'r/3R)) \\ \times (3 \cos^2 \Theta - 1) / (81) (6\pi)^{1/2} \quad (7)$$

where the Z and Z' are scaling parameters that determine the extent of the wave function.

2.2 Stressed crystals

Uniaxial stress divides the atoms at different angles to the stress field into several classes having different a - and B -shifts. Each of these classes must be considered separately. We will denote the a - and B -shifts of

each of these classes by an angle subscript which is the angle between the stress axis and the interaction direction of the class of atoms under consideration.

It is convenient to express the stress dependence of the nearest neighbor hfi constants as a sum of terms proportional to the local strain symmetries. Since the stress one can apply within the elastic limit of an alkali halide is quite small, we may assume Hooke's Law. This means that the local elastic compliance constants, S'_{ij} , can be related to those for the bulk crystal, S_{ij} , by the relation

$$S'_{ij} = k_{ij} S_{ij}. \quad (8)$$

The linear combinations of these elastic compliance constants that reflect the various symmetries of the distortion caused by the stresses applied in this experiment are shown in Table 1[8, 9]. Γ_1 is the spherically symmetric or cubic distortion (volume change), Γ_3 is the tetragonal distortion along the z -axis, (two opposite sides of a cube move two units while the remaining four sides move in the opposite direction by one unit), and Γ_5 is the rhombic distortion (a change in the angle between the crystalline axes)[10]. From this one can show[8] that the a -shifts that we expect to measure for the different classes of first shell ions and the different stress axes used can be written as

Stress along [100]

$$\delta a_{\parallel} = \delta a_1 + 2\delta a_3 \quad (9)$$

$$\delta a_{\perp} = \delta a_1 - \delta a_3 - A_3. \quad (10)$$

Table 1. Relative amounts of distortion for the different stress cases

Symmetry	[100] Stress	[110] Stress	[111] Stress	Hydrostatic pressure
Γ_1	$S_{11} + 2S_{12}$	$S_{11} + 2S_{12}$	$S_{11} + 2S_{12}$	$3(S_{11} + 2S_{12})$
Γ_3	$2(S_{11} - S_{12})$	$-(S_{11} - S_{12})$		
Γ_5		$3S_{44}/2$	S_{44}	

Stress along [110]

$$\delta a_{\perp} = \delta a_1 - \delta a_3 + \frac{1}{2}A_3 \quad (11)$$

$$\delta a_{45} = \delta a_1 + \frac{1}{2}\delta a_3 + \frac{1}{2}A_3. \quad (12)$$

Stress along [111]

$$\delta a_{55} = \delta a_1 + A_5/3 \quad (13)$$

where

$$\delta a_1 = \frac{PR}{3} (S'_{11} + 2S'_{12}) \frac{\partial a}{\partial z} \quad (14)$$

$$\delta a_3 = \frac{PR}{3} (S'_{11} - S'_{12}) \frac{\partial a}{\partial z}, \quad (15)$$

R is the nearest neighbor distance, P the pressure, the S'_{ij} are the local elastic compliance constants, δa_1 is the a -shift caused by distortions of Γ_1 symmetry and δa_3 is caused by distortions of Γ_3 symmetry. Although Γ_5 type distortion is present for stress along the [110] and [111] axes this should have no first order effect on the a -shift of the first shell ions. This follows from the symmetry of the site which demands that a rotation by $\delta\theta$ produce an a -shift equal that of a rotation of $-\delta\theta$ or that the ion is at an extremum with respect to the angle of the axes. The terms involving A_3 and A_5 are due to core distortions which will be explained in Section 5. If these core distortions are not present A_3 and A_5 become equal to zero.

3. THE EXPERIMENT

The goal of this study was to measure the change in the hfi constants of the F -center resulting from uniaxial stress. An accurate measurement of the hfi constants requires the use of ENDOR. As the ENDOR technique has not been previously used to study stressed crystals, new techniques and equipment had to be developed.

The ENDOR method, introduced by Feher [11], consists of saturating an EPR transition of an inhomogeneously broadened line and simultaneously irradiating with a fre-

quency capable of causing transitions between the hyperfine sublevels. The EPR resonance is monitored and an indication is observed when ENDOR transitions occur due to temporary partial desaturation of the EPR signal.

The actual equipment used to detect the power absorption at resonance has been described elsewhere [12]. In the magnetic fields at which we work ($H \approx 3000$ G) the frequency, f_{ENDOR} , is typically between 0.5–50 MHz. The actual experimental techniques have been described elsewhere [13].

At X -band the EPR techniques require that the samples be placed in microwave cavities. This poses the problem that besides the microwave field, an r.f. field and a method of putting stress on the crystal all must be introduced into the cavity at low temperature without destroying the cavity Q . Moreover both the microwave and r.f. fields have to be perpendicular to the external field H .

As the observed frequency shifts are small, it was necessary to take our data at points where any rotation of the crystal under stress will cause a minimum of frequency shift. Thus all data was taken at points where the change in f_{ENDOR} as a function of crystal orientation is zero or at points at where two lines cross so that rotation will only cause a line broadening.

When stress is applied to a crystal the symmetry of the F -center site is changed. For example, the first shell hfi has cylindrical symmetry before stress but generally after stress this is removed. In addition, atoms at different angles with respect to the stress axis will see different local changes in the fields and thus must be investigated separately. This means that for each class of ions about the stress axis we must usually measure the line shift of at least three different lines in order to determine the δa and two of the δB 's. Only two of the δB 's are needed as the sum $\delta B_{xx} + \delta B_{yy} + \delta B_{zz}$ equals zero. Only in the case of those first shell ions lying in the direction parallel to stress applied along a

[100] axis is the cylindrical symmetry retained. Furthermore stress along the [100], [110] and [111] crystal axes gives different combinations of cubic, Γ_1 , tetragonal, Γ_3 , and rhombic, Γ_5 , distortion. Thus stress along these three directions is needed to determine how each of these three distortions effects the observed results.

All these conditions made it necessary to build two different cavities in order to be able to apply stress at enough different angles to the magnetic field. These two cavities are shown in Fig. 1.

The cylindrical cavity is filled with teflon to reduce its dimensions to a size that will fit into a liquid N_2 dewar. As this cavity operates in the TE_{011} mode the sample is placed along the cavity axis. The ENDOR power is introduced by means of rectangular coils placed in a square configuration on either side of the sample. Pressure is applied to the sample by weights hanging on a lever arm through a stainless steel rod and teflon plunger to the

inside of the cavity. Teflon is pliable enough to give a uniform pressure distribution over the top of the sample provided care is taken to cut the ends of the samples squarely and to align the sample properly in the cavity.

In the rectangular cavity the pressure is applied to the sample by similar methods with the addition of an L-shaped arm to change the direction of pressure inside the dewar system. In this case the teflon plunger passes through a brass tube extending out from the center of the broad side of the cavity. This tube acts both as a guide for the plunger and as a waveguide beyond cut-off. The center section of the cavity is slit vertically through the center of the broad side containing the tube and insulated from the two end sections. This allows the center wall section itself to be used as the first turn of a four turn ENDOR coil wrapped around the outside of the cavity.

The mechanical advantages of the lever systems were determined by precise measurement of the dimensions involved. These agreed

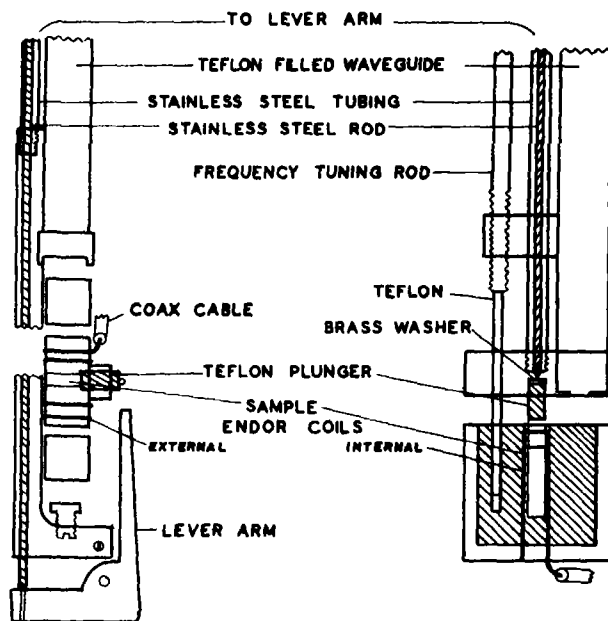


Fig. 1. Microwave cavities used to apply stress to the samples.

with those obtained from micrometer measurements of displacements of the weights versus that of the teflon plungers.

As the observed frequency shifts were quite small special procedures were developed to measure these shifts. The frequency of the center of the ENDOR line cannot be determined to the accuracy required in this experiment. This is because line widths and noise make it impossible to measure the center of the line to 1 part in 10^4 as required. We can however put accurate frequency markers on the recorder charts by marking the beats between the ENDOR oscillator and a reference oscillator (BC-221) calibrated against *WWV*. In analysing the data a fiducial mark is put on each ENDOR line in an unstressed run. Then all further runs are compared with this run as follows: The position of each line is determined by a 'best' fit between the line in the run under consideration and that of the unstressed run by a comparison of the two curves on a lighted tracing box. When this position is determined a mark is placed on the stressed line graph coinciding with that on the unstressed graph. The two charts are then lined up to give a best fit with the standard frequency markers. The distance between the two marks on the stressed and unstressed lines is then measured and the frequency shift determined from a linear interpolation of the distance between two known frequency markers. This method thus performs two averages: (1) over peak position due to random noise fluctuations and (2) over standard frequency markers which have a little scatter because of different reaction times between hearing of the zero beat and the pressing of the button to put a mark on the chart recorder.

All frequency shifts were then determined by a least squares fit of the data points to a straight line. All errors given are the standard deviations in slope obtained in this fitting procedure.

Samples of KCl, KBr and LiF were obtained from Harshaw Chemical Co. *F*-centers were produced in LiF by X-raying the samples

for about 100 hr. In KCl both additive coloration and X-raying were used to produce the *F*-centers in the initial studies. As both methods gave the same stress data to well within experimental error all later data was taken on additively colored crystals where large densities of *F*-centers are easily obtained. Additive coloration also was used in the case of KBr.

4. RESULTS

In Tables 2-4 we give the actual frequency shifts per unit stress (in kHz/kg/mm²) for each of the various lines measured. To identify these lines we also give there the stress angle (defined as the angle between the stress axis and the *z*-axis of the unstressed anisotropic *hfi* tensor) and the direction cosines between the external magnetic field and the anisotropic *hfi* tensor (h_x , h_y , and h_z). The principal axes of the anisotropic interaction are hard to depict but in every case the *z*-axis is chosen to be the axis between the center of the vacancy and the ion under investigation. The *x*-axis is chosen to be the axis perpendicular to this that points as nearly as possible in the direction of stress. The *y*-axis is the remaining perpendicular axis. The shift in *hfi* (combination of δa and δB 's) also listed in these tables is calculated assuming there is no rotation of the *hfi* axes, i.e. h_x , h_y , h_z remain constant under stress.

The values of frequency shift given are in many cases the average of many separate runs on different samples. In all cases the different runs gave results that agree well within the standard deviation quoted. A plot of a typical run for the ions parallel to stress along the [100] axis is shown in Fig. 2.

The *a*- and *B*-shifts per unit stress calculated from the measured data using the equations for the change in the *hfi* given in Tables 2-4 are shown in Tables 5-9. Also given in these Tables are values of the average *a*-shift, $\langle \delta a \rangle$, defined as

$$\langle \delta a \rangle = \left(\sum_a N_a \delta a_a \right) / \sum_a N_a \quad (16)$$

Table 2. Measured frequency shifts per unit stress (kHz/kg/mm²) for first shell ions

Stress angle	h_x	h_y	h_z	Hf_i	LiF	KCl	KBr
Stress along [100]							
0°			$\theta = 90^\circ$	$\delta a/2 - \delta b/2$	10.9 ± 0.9	15.0 ± 1.0	15.5 ± 1.7
0°			$\theta = 0^\circ$	$\delta a/2 + \delta b$	19.2 ± 1.7	16.5 ± 2.6	25.3 ± 3.0
90°	0	0	1	$\delta a/2 + \delta B_{xx}/2$	-7.5 ± 9	-7.3 ± 1.2	-4.0 ± 1.3
90°	0	$\sqrt{1/2}$	$\sqrt{1/2}$	$\delta a/2 - \delta B_{xx}/4$	-3.7 ± 1.0		
90°	1	0	0	$\delta a/2 + \delta B_{xx}/2$	-0.4 ± 4.0	-12.0 ± 2.0	-13.6 ± 2.0
90°	$\sqrt{1/2}$	$\sqrt{1/2}$	0	$\delta a/2 - \delta B_{xx}/4$	0.2 ± 12.0	0.6 ± 1.5	-0.4 ± 3.5
Stress along [110]							
45°	0	1	0	$\delta a/2 + \delta B_{yy}/2$		4.6 ± 1.0	3.5 ± 1.3
45°	$\sqrt{1/2}$	0	$\sqrt{1/2}$	$\delta a/2 - \delta B_{yy}/4$		3.2 ± 0.7	3.6 ± 1.7
45°	0	0	1	$\delta a/2 + \delta B_{zz}/2$		7.1 ± 1.5	
90°	0	0	1	$\delta a/2 + \delta B_{zz}/2$		-4.4 ± 0.8	-2.5 ± 1.0
90°	0	1	0	$\delta a/2 + \delta B_{yy}/2$		-3.6 ± 0.8	-1.9 ± 1.6
90°	1	0	0	$\delta a/2 + \delta B_{xx}/2$		-5.0 ± 1.2	
Stress along [111]							
55°	$1/2$	$1/2$	$\sqrt{1/2}$	$\delta a/2 + \delta B_{xx}/8$		1.5 ± 0.5	
55°	0	1	0	$\delta a/2 + \delta B_{yy}/2$		1.4 ± 0.3	
55°	$1/\sqrt{3}$	0	$2/\sqrt{6}$	$\delta a/2 + \delta B_{xx}/3 + \delta B_{xx}/6$		1.4 ± 0.4	
55°	$\sqrt{1/2}$	$3/\sqrt{12}$	$1/\sqrt{6}$	$\delta a/2 + \delta B_{xx}/24 + \delta B_{yy}/3$		2.2 ± 0.3	
55°	$2/\sqrt{6}$	0	$1/\sqrt{3}$	$\delta a/2 + \delta B_{xx}/3 + \delta B_{xx}/6$		2.0 ± 1.7	

where δa_α is the a -shift for the class of nuclei at an angle α to the stress direction and N_α is the number of nuclei in this class.

5. DISCUSSION

5.1 First shell KCl

When comparing the a -shifts (δa 's) with the motion of the bulk crystal predicted by the elastic constants we see that whenever the elastic constants indicate an inward motion (a decrease in distance between nearest neighbors) we find a positive δa and wherever an increase in nearest neighbor distance is indicated a negative δa is found. In the section on theory it was stated that the a -value is proportional to the square of the wave function evaluated at the nucleus under study. This means that a positive δa can be explained as an increase in the F -center electron wave function at the nucleus caused principally by a decrease in the nearest neighbor distance. Similar reasoning leads to the conclusion that

a negative δa means an increase in the nearest neighbor distance. We thus conclude that the motion of the nuclei around the F -center vacancy is in the same direction as the motion of the nuclei in the bulk crystal. This is in conflict with the conclusion reached by Gebhardt and Maier[3] that the local s_{12} is of opposite sign from that in the bulk crystal. Schnatterly[4] has questioned the assumptions needed for their conclusions. Furthermore, it can be shown[8] that a spherical hole in an isotropic medium moves in the same direction and with twice the magnitude of the motion of the bulk medium. To be sure the alkali halides are not isotropic, but even so a motion in the opposite direction would mean that the potential of the F -center would have to be rather unique.

For the bulk crystal, the three stress cases [100], [110] and [111] have the same cubic distortion. The assumption of a linear shift of a with stress is verified from the experimental

Table 3. Measured frequency shifts per unit stress (kHz/kg/mm²) for second shell ions

Stress angle	h_x	h_y	h_z	Hfi	KCl	KBr
Stress along [100]						
45°	0	1	0	$\delta a/2 + \delta B_{yy}/2$		
45°	1	$\sqrt{1/2}$	$\sqrt{1/2}$	$\delta a/2 + \delta B_{yy}/8$	-1.4 ± 0.5	-2.2 ± 1.2
45°	$\sqrt{1/2}$	0	$\sqrt{1/2}$	$\delta a/2 - \delta B_{yy}/4$	0.9 ± 1.0	
90°	0	0	1	$\delta a/2 + \delta B_{zz}/2$	-3.0 ± 0.4	-10.0 ± 1.4
90°	0	1	0	$\delta a/2 + \delta B_{yy}/2$	-1.5 ± 0.2	-5.9 ± 1.1
90°	1	0	0	$\delta a/2 + \delta B_{xx}/2$	-0.7 ± 1.1	
Stress along [110]						
0°	1	0	0	$\delta a/2 + \delta B_{xx}/2$	4.5 ± 0.4	
0°	.98	.19	0	$\delta a/2 + 0.10\delta B_{yy} + 0.48\delta B_{xx}$	6.0 ± 0.3	
0°	.57	.82	0	$\delta a/2 + 0.33\delta B_{yy} + 0.16\delta B_{xx}$	4.0 ± 0.3	
0°	.42	.91	0	$\delta a/2 + 0.42\delta B_{yy} + 0.08\delta B_{xx}$	3.4 ± 0.4	
0°	0	0	1	$\delta a/2 + \delta B_{zz}/2$	9.6 ± 0.9	
60°	0	$\sqrt{1/2}$	$\sqrt{1/2}$	$\delta a/2 - \delta B_{xx}/4$	-1.0 ± 0.2	
60°	$\sqrt{1/6}$	$\sqrt{1/12}$	$3/\sqrt{12}$	$\delta a/2 - \delta B_{xx}/24 + \delta B_{zz}/3$	-0.6 ± 0.3	
60°	1	0	0	$\delta a/2 + \delta B_{xx}/2$	-0.6 ± 0.7	
60°	$\sqrt{1/2}$	$1/2$	$1/2$	$\delta a/2 + \delta B_{xx}/8$	-0.6 ± 0.3	
90°	0	0	1	$\delta a/2 + \delta B_{zz}/2$	-7.9 ± 0.8	
90°	1	0	0	$\delta a/2 + \delta B_{xx}/2$	-8.4 ± 0.9	
90°	.98	.17	0	$\delta a/2 + 0.49\delta B_{xx} + 0.02\delta B_{yy}$	-10.5 ± 0.7	
90°	.57	.82	0	$\delta a/2 + \delta B_{xx}/6 + \delta B_{yy}/3$	-8.5 ± 0.6	
Stress along [111]						
35°	0	1	0	$\delta a/2 + \delta B_{yy}/2$	2.6 ± 0.2	
35°	$\sqrt{1/6}$	$3/\sqrt{12}$	$\sqrt{1/12}$	$\delta a/2 + \delta B_{xx}/24 + \delta B_{yy}/3$	2.4 ± 0.2	
35°	$2/\sqrt{6}$	0	$2/\sqrt{12}$	$\delta a/2 + \delta B_{xx}/3 + \delta B_{zz}/6$	2.5 ± 0.2	
35°	$\sqrt{1/3}$	0	$2/\sqrt{6}$	$\delta a/2 + \delta B_{xx}/6 + \delta B_{zz}/3$	5.2 ± 0.8	
90°	0	0	1	$\delta a/2 + \delta B_{zz}/2$	-3.1 ± 0.3	
90°	$\sqrt{1/12}$	$\sqrt{1/6}$	$3/\sqrt{12}$	$\delta a/2 + \delta B_{yy}/8 + 3\delta B_{xx}/8$	-3.0 ± 0.3	
90°	$2/\sqrt{12}$	$2/\sqrt{6}$	0	$\delta a/2 + \delta B_{yy}/3 + \delta B_{xx}/6$	-3.3 ± 0.3	
90°	$2/\sqrt{6}$	$\sqrt{1/3}$	0	$\delta a/2 + \delta B_{xx}/3 + \delta B_{yy}/6$	-5.7 ± 0.4	

Table 4. Frequency shift per unit stress for the fourth shell lines when stress is along [110]

Stress angle	h_x	h_y	h_z	Hfi	KBr
45	0	1	0	$\delta a/2 + \delta B_{yy}/2$	-0.1 ± 1.6
45	$\sqrt{1/2}$	0	$\sqrt{1/2}$	$\delta a/2 + \delta B_{yy}/4$	0.5 ± 1.5
90	0	0	1	$\delta a/2 + \delta B_{zz}/2$	-1.6 ± 1.4
90	0	1	0	$\delta a/2 + \delta B_{yy}/2$	-0.7 ± 1.5

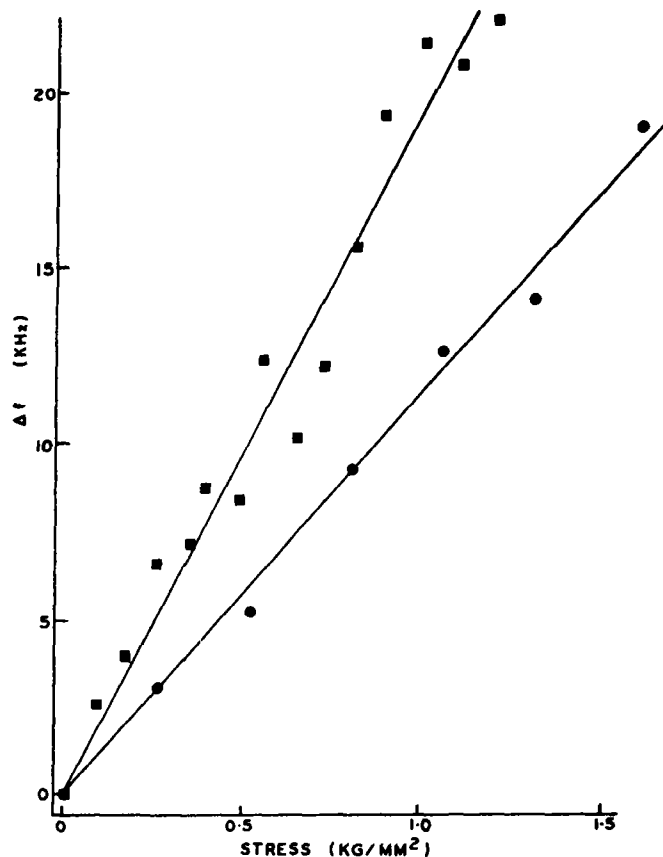


Fig. 2. Plot of the frequency shift vs. stress for the two first shell lines of KCl when stress is applied along a [100] axis.

Table 5. *a*- and B-shifts per unit stress (kHz/kg/mm²) for first shell ions in LiF when stress is along [100]

$\delta a_{ }/h\delta P$	$\delta a_{\perp}/h\delta P$	$\delta a/h\delta P$	$\delta b_{ }/h\delta P$	$\delta B_{xx_{\perp}}/h\delta P$	$\delta B_{xx_{\perp}}/h\delta P$	$\delta B_{xx_{\perp}}/h\delta P$
27.4 ± 1.6	-5.2 ± 3.0	5.7	5.4 ± 1.3	4.4 ± 7.2	5.4	-9.8 ± 3.6

data. The average *a*-shift due to tetragonal distortion due to linear motional effects is zero (the total inward motion equals the total outward motion). Any rhombic distortion (rotation of the crystal axes) should produce zero-*a*-shift to first order. Thus only cubic distortion should have any effect on the aver-

age *a*-shifts, $\delta a/(h\delta P)$'s as defined in (16). This means that the average *a*-shifts should be the same for all three stress cases [100], [110] and [111] as the magnitude of the cubic distortion is the same in all cases. From Table 6 this is seen *not* to be the case, but rather they are 7.6, 2.0 and 3.4 kHz/kg/mm² respectively.

Table 6. *a*- and *B*-shifts per unit stress (kHz/kg/mm²) for the first shell ions of KCl

	Stress [100]	Stress [110]	Stress [111]
$\delta a_{ }/(h\delta P)$	30.9 ± 2.1		
$\delta a_{\perp}/(h\delta P)$	-4.1 ± 2.1	-8.7 ± 1.1	
$\delta a_{45^\circ}/(h\delta P)$		7.3 ± 1.1	
$\delta a_{35^\circ}/(h\delta P)$			3.4 ± 0.9
$\delta a/(h\delta P)$	7.6	2.0	3.4
$\delta b_{ }/(h\delta P)$	1.0 ± 1.9		
$\delta B_{xx}/(h\delta P)$	-22.6 ± 4.6	-1.4 ± 2.8	
$\delta B_{yy}/(h\delta P)$	33.1	1.4 ± 2.5	
$\delta B_{zz}/(h\delta P)$	-10.5 ± 3.1	0.0 ± 2.5	
$\delta B_{xx45^\circ}/(h\delta P)$		-8.7	
$\delta B_{yy45^\circ}/(h\delta P)$		1.9 ± 1.6	
$\delta B_{zz45^\circ}/(h\delta P)$		6.8 ± 2.9	
$\delta B_{xx35^\circ}/(h\delta P)$			1.0
$\delta B_{yy35^\circ}/(h\delta P)$			-0.6 ± 1.0
$\delta B_{zz35^\circ}/(h\delta P)$			-0.4 ± 1.0

Table 7. *a*- and *B*-shifts per unit stress (kHz/kg/mm²) for the first shell ions of KBr

	Stress [100]	Stress [110]
$\delta a_{ }/(h\delta P)$	37.5 ± 3.1	
$\delta a_{\perp}/(h\delta P)$	-3.2 ± 3.5	-4.4 ± 1.9
$\delta a_{45^\circ}/(h\delta P)$		3.2
$\delta a/(h\delta P)$	10.5	3.2
$\delta b_{ }/(h\delta P)$	6.5 ± 2.3	
$\delta B_{xx}/(h\delta P)$	-24.0 ± 10.4	~ 0
$\delta B_{yy}/(h\delta P)$	28.8	~ 0
$\delta B_{zz}/(h\delta P)$	-4.8 ± 4.8	~ 0
$\delta B_{xx45^\circ}/(h\delta P)$		
$\delta B_{yy45^\circ}/(h\delta P)$		0.0
$\delta B_{zz45^\circ}/(h\delta P)$		

values should be the same. The measured values of -4.1 ± 2.1 and -8.7 ± 1.1 cannot be equated to within experimental error. These internal inconsistencies point to the presence of an additional effect. The corresponding measurements of the anisotropic interaction constant suggest the resolution of the difficulty.

The large *B*-shifts seen for those ions perpendicular to [100] stress and also for those at 45° to [110] stress indicate that a change in the anisotropy of the ion core functions is taking place. This means that the applied stress causes a distortion of the ion cores. Such a distortion will cause a change in the orthogonalization of the *F*-center envelope wave function to the core. Using (5) we find that

$$d(|\Psi_F|^2) = |\Phi_F|^2 dA + Ad(|\Phi_F|^2). \quad (17)$$

These differences cannot be explained by experimental error. Another example of the difficulty of motional effects alone to explain the uniaxial stress data is for those ions perpendicular to stress along the [100] and [110] axes. Elasticity theory indicates the measured

This means that an *a*-shift can arise either from a change in the envelope function or a change in the amplification factor. Thus we must allow for the effect of a possible change of the amplification factor in (9-13). The only cases where tetragonal ion core distortion

Table 8. *a*- and B-shifts per unit stress (kHz/kg/mm²) for the second shell ions of KCl

	Stress [100]	Stress [110]	Stress [111]
$\delta a_{ }/(h\delta P)$		11.7 ± 0.8	
$\delta a_{40^\circ}/(h\delta P)$		-1.5 ± 0.6	
$\delta a_{\perp}/(h\delta P)$	-3.5 ± 0.8	-16.8 ± 0.8	-8.1 ± 0.6
$\delta a_{35^\circ}/(h\delta P)$			6.8 ± 0.8
$\delta a_{45^\circ}/(h\delta P)$	-1.3 ± 1.3		
$\delta a/(h\delta P)$	-2.0	-1.8	-0.7
$\delta B_{xx'}/(h\delta P)$		-2.6 ± 1.2	
$\delta B_{yy'}/(h\delta P)$		-4.8 ± 1.2	
$\delta B_{zz'}/(h\delta P)$		7.6 ± 2.0	
$\delta B_{xx'}/(h\delta P)$	2.2 ± 2.2	-0.2 ± 1.6	-8.0 ± 5.0
$\delta B_{yy'}/(h\delta P)$	-0.4 ± 1.2	-0.6	$+6.2$
$\delta B_{zz'}/(h\delta P)$	-2.4 ± 1.6	0.8 ± 1.5	1.8 ± 1.2
$\delta B_{xx'}/(h\delta P)$		1.2 ± 4.0	
$\delta B_{yy'}/(h\delta P)$		-1.5	
$\delta B_{zz'}/(h\delta P)$		0.3 ± 1.8	
$\delta B_{xx'}/(h\delta P)$			-7.6
$\delta B_{yy'}/(h\delta P)$			-1.6 ± 1.2
$\delta B_{zz'}/(h\delta P)$			9.2 ± 7.0
$\delta B_{xx'}/(h\delta P)$			
$\delta B_{yy'}/(h\delta P)$	-6.0 ± 4.4		
$\delta B_{zz'}/(h\delta P)$			

Table 9. *a*- and B- shifts per unit stress along [110] for fourth shell KBr ions (kHz/kg/mm²)

$\delta a_{45^\circ}/h\delta P$	$\delta a_{\perp}/h\delta P$	$\delta a/h\delta P$
0.4	-2.3	-0.5

can have much effect is for those ions perpendicular to stress along [100] and those at 45° to stress along [110]. In these two cases the K^+ ion feels tetragonal effects due to the motion of neighboring Cl^- ions. This motion is one-half the magnitude and of opposite sign for those atoms at 45° as compared to those perpendicular to stress. For the stress along the [110] axis those atoms perpendicular to stress will have Γ_3 type core distortion due to the rotation of the four neighboring Cl^- ions. This last effect will also be present for all

the atoms when stress is applied along the [111] axis. We thus add the terms in A_3 and A_5 to equations (9)–(13) where A_3 and A_5 are the *a*-shifts caused by core distortions of Γ_3 and Γ_5 symmetry respectively. There is one more equation than is necessary to solve for the quantities listed so we have an internal check on the consistency of the data when done. We solve these by using the fact that

$$3(\delta a_{[100]}) + 6(\delta a_{[110]}) = 9\delta a_1 + A_5 \quad (18)$$

combining this with (13), (9) and (10) gives $\delta a_1 = 4.1$, $A_5 = 2.1$, $\delta a_3 = 13.4$ and $A_3 = 5.2$. If on the other hand we use the above values of δa_1 and A_5 and use (11) to solve for δa_3 we find $\delta a_3 = +11.8$. These two values of δa_3 should be equal and the near equality provides an internal consistency check. The fact that the two values are not quite equal

gives an indication of the error in our data. For future calculations we will use the average of these two (12.6 kHz/kg/mm²).

Our value for $\delta a_1/(h\delta p) = 4.1$ kHz/kg/mm² agrees quite favorably with that of Liu[14] who obtained a value of 4.2 kHz/kg/mm² (a temperature correction has been made) from hydrostatic pressure data which gives pure cubic distortion. The small effect of Γ_5 distortion required is expected from the results of Hetrick and Compton[15] who observed the luminescence of the excited *F*-center under uniaxial stress. They interpret their results as shifts in the ground state energy level of the *F*-center and find that they see no effect due to rhombic distortions.

5.2 Comparison of first shell data

In Table 10 we compare the calculated values of δa_1 , δa_3 , A_3 , and A_5 for KCl with those found for LiF and KBr. As we have only [100] stress data for LiF, the $\delta a_1/(h\delta p)$ found

Table 10. Contributions to $\delta a_{\text{meas.}}$ per unit stress. (kHz/kg/mm²)

	LiF	KCl	KBr
$\delta a_1/(h\delta p)$		4.1	3.6
$\delta a_1/(h\delta p)$ (Liu[35])	1.2	4.2	3.5
$\delta a_3/(h\delta p)$	13.1	12.6	16.9
$A_3/(h\delta p)$	-6.7	-5.2	-10.1
$A_5/(h\delta p)$		-2.1	17.8

by Liu[14] is used to separate the various terms in Table 10. In the case of KBr only stress data for the [100] and [110] axes has been taken. This is just enough to separate the various terms listed. Although we do not have an internal consistency check of the data, an external check remains and the agreement between our value of δa_1 and that of Liu gives us confidence in the results.

It is useful to present these results in a form independent of the properties of the host crystal. To eliminate the effects of the different amplification factors for the Li⁺ and K⁺ ions we can express the quantities of Table 10

as relative *a*-shifts, i.e. divide by the unstressed *a*-value. The different elastic properties of the various samples can be eliminated by dividing the above quantities by the appropriate components of bulk crystal strain obtaining relative frequency shifts per unit of relative ($\delta R/R$) strain. That is, we have divided effects due to cubic distortion by $(s_{11} + 2s_{12})/3$, effects due to tetragonal distortions by $(s_{11} - s_{12})/3$, and effects due to rhombic distortions by s_{44} . The results of this reduction procedure are shown in Table 11.

Table 11. Sensitivity of various terms given by relative frequency shifts per unit of relative strain

	LiF	KCl	KBr
Cubic motion	1.96	3.55	3.12
Tetragonal mot.	8.38	7.9	9.83
Tet. core dist.	-4.28	-3.20	-5.95
Trig. core dist.		-0.14	1.03

It should be noted from the results in this reduced form that the relative sensitivity per unit strain for motion of tetragonal symmetry is nearly constant for all three alkali halides studied. This same regularity is seen in the core distortion caused by tetragonal strain. In both KCl and KBr the sensitivity to rhombic strain is quite small. The sensitivity to cubic motion for LiF seems to be quite different from that in KCl and KBr. In addition a negative *a*-shift with hydrostatic pressure has been seen for the first shell in LiCl[16]. However Li salts are peculiar in several ways. Two possible explanations can be presented.

The possibility that cubic distortions can cause changes in the amplification factors should be considered. Liu's data indicates that the ratio of *B*-shift to *a*-shift is biggest for LiF and smallest for KCl. We have said in our previous analysis that a large *B*-shift indicates a change in the amplification factor. If the amplification does change with cubic distortion the indicated cubic sensitivity in Table 11 does not reflect a true estimate of

the effect of motion. Indeed the sensitivity due to tetragonal motion may be a much better indication of the true value as the change in amplification factor due to tetragonal distortion has been eliminated from this number. An argument against this explanation is that although the ratio of *a*- to *B*-shift changes considerably among the samples studied, the relative *B*-shift ($\delta b/b$) is not that different for any of the crystals.

The second explanation is based on the assumption that the neighboring ions relax into the negative ion vacancy. Feuchtwang [17] on the basis of displacements required to explain the observed quadrupole splittings estimates that this relaxation may be as much as 10 per cent of the lattice spacing. The inward relaxation in the Li salts may well be large enough to allow displacement of the second shell ions with stress without moving the first shell ions very much. This would explain the small *a*-shift seen for the Li salts.

If these differences between host crystals are ignored the observed *a*-shifts can be analysed in terms of two distinct simple models. The first model interprets the whole *a*-shift as resulting completely from the motion of the neighboring ions while the second using an admixture of wave function argument pretends there is no motion of the ions and all of the *a*-shift arises because of an admixture of wave functions of the correct symmetry. These are two extreme cases and the actual state of affairs is probably a combination of both. By ignoring one or the other we can get limiting values for the two cases.

5.3 Ionic motion

Seidel has shown that the *a*-value for the first shell in going from one crystal to the next obeys the rule

$$a = \text{constant} (1/R^3) \quad (19)$$

where *R* is the nearest neighbor distance. We now make the assumption that this law is valid for stress induced changes in the nearest

neighbor distance. This means that the relative *a*-shift with pressure equals the relative local volume change or

$$\frac{\delta a_1}{a} = -\frac{dV}{V_{\text{Local}}} = -\frac{3 dr}{r_{\text{Local}}} \quad (20)$$

Using (20) the ratio between the local volume change and that of the bulk crystal (equal to $s_{11} + 2s_{12}$) can be determined. They are shown in Table 12. In a similar manner the ratio of local tetragonal motion to that in the bulk is

$$\left(\frac{\delta a_3}{a}\right)/(s_{11} - s_{12}) = \frac{d(\text{Tet. Mot.})_{\text{Local}}}{d(\text{Tet. Mot.})_{\text{Bulk}}} \quad (21)$$

These are given in Table 12.

Table 12. Analysis of data using Seidel's Rule

		LiF	KCl	KBr
	Our	0.65	1.18	1.06
$\frac{dV_{\text{Local}}}{dV_{\text{Bulk}}}$	B&N [23]		1.26	1.16
	Our	2.79	2.75	3.28
$\frac{d\text{TET}_{\text{Local}}}{d\text{TET}_{\text{Bulk}}}$	B&N [23]		1.45	1.26
k_{11}		2.4	2.2	2.6
k_{12}		4.2	5.9	8.0

The local elastic constants s'_{11} , s'_{12} can be related to those of the bulk material s_{11} , s_{12} by equation (8). These relations combined with (20) give the values of k_{11} and k_{12} shown in Table 12.

From Table 12 it is seen that the local volume change is about equal to that in the bulk sample in the case of KCl and KBr. This is in disagreement with the results predicted by the optical studies of Jacobs [2] on the *F*-center under hydrostatic pressure. His results indicate that locally it is about twice as compressible as for the bulk material. This factor of two is predicted by a spherical hole in an iso-

tropic medium. The calculation of Davitashvili and Politov[18] indicates that local compressibility of all crystals with a rock salt lattice should be 1.946 times that of the bulk crystal. The optical work obtains this value of about 2 by the use of the empirical Ivey Law[19]. Buchenauer and Fitchen[20] have had to modify this equation to take in ion-size effects. (CsF data would have indicated an expansion with increasing pressure.) In any case the optical work presents a different problem as the effects of pressure on both the ground and excited states have to be considered. Using the change with hydrostatic pressure of the resolved *hf* splittings of the EPR line in LiF Blum[21] finds that in this sample the local compressibility is 1.5 times that of the bulk crystal. However, in LiF these splittings are caused primarily by the second shell *hfi*, and Liu[14] has found the second shell in LiF has a negative *a*-shift. Because of the differences in sign of the pressure effect on the first two shells in LiF it will make Blum's results difficult to interpret.

Benedek and Nardelli[22,23] have analyzed the Raman spectra of *F*-centers in KCl and KBr. In their second paper[23], they find expressions for the local elastic constants c'_{ij} . From these we calculate the ratio of local to bulk volume change shown in Table 12 (they are listed as *B&N*). There is excellent agreement between our results and theirs. The fact that their ratio of local to bulk tetragonal motion, Table 12, is much smaller than ours is probably an indication of how much wave function of tetragonal symmetry is being admixed in by the uniaxial stress.

That our data indicates the *F*-center is not much more compressible than the bulk crystal (and in the case of LiF and LiCl even less compressible) is a little surprising. This may well be experimental indication that the nearest neighbors have moved into the vacancy as previously predicted[17]. The overlap forces due to the Pauli exclusion principle between the core electrons would then make the near-

est neighbors less compressible than a simple spherical cavity.

Both k_{11} and k_{12} are found to be positive. This is just another way of saying that the local motion is proportional to and in the same direction as that in the bulk crystal. $K_{11} = 2.5$ means that the motion along the stress axis is up to 2.5 times larger than that in the bulk sample. A $k_{12} = 6.0$ means that the motion perpendicular to stress is up to 6 times that in the bulk crystal. Although the inward motion along the stress axis seems reasonable the outward motion at first thought seems quite large. Remembering that Feuchtwang[17] finds an inward relaxation of the ions around the vacancy of up to 10 per cent of the lattice spacing, a computation of our maximum outward displacement is useful. This shows a maximum displacement outward of about 0.03 per cent of the lattice spacing. Thus the $k_{12} = 6$ need not imply that the whole crystal is strained by this amount but rather only the nearest ions that have relaxed into the vacancy and thus are probably much more loosely coupled to the rest of the lattice.

5.4 The admixture of D-state wave functions

As stated previously a distortion of the lattice will admix into the envelope function a function with the symmetry of the distortion. Let Φ_s represent the spherically symmetric *F*-center envelope wave function before stress. Letting Φ_D represent a wave function with the same symmetry as the distortion, the *F*-center envelope function becomes

$$\Phi_F = (1 - \alpha^2)^{1/2} \Phi_s + \alpha \Phi_D \quad (22)$$

where α is linear in stress ($\alpha = 0$ when the stress is zero). Using (3), (5) and (22) and only keeping terms linear in α one finds

$$a + \delta a = 8\pi g_e \beta_e g_n \beta_n A [|\Phi_s|^2 + 2\alpha \Phi_s \Phi_D]/3. \quad (23)$$

Using (23) the admixture coefficient for tet-

ragonal motion is found to be

$$\alpha = \frac{1}{2}(\delta a_3/a) (\Phi_s/\Phi_D). \quad (24)$$

As stated previously we take the envelope wave functions to be of the hydrogen type. Thus we let $\Phi_s = u_{100}$ and $\Phi_D = u_{320}$. See equations (6) and (7). For the ground state wave functions we will use the scaling parameters computed by Gourary and Adrian[7]. They are listed as Z in Table 13. The scaling parameter, Z' , for the D -function is unknown. We compute the admixture coefficient for three cases $Z = Z'$, $Z' = 6.0$ (the maximum of the D -function is placed at the nearest neighbors), and $Z' = 10.5$ (the maximum amount of wave function is placed at the nearest neighbors). The admixture coefficients computed using the values of Z' are shown in Table 13.

Table 13. Admixture coefficients for the d -state wave functions

	Z	Z'	α
LiF	1.71	1.71	3.6×10^{-3}
		6.0	1.9×10^{-4}
		10.5	1.2×10^{-4}
KCl	1.99	1.99	4.1×10^{-4}
		6.0	3.4×10^{-4}
		10.5	2.2×10^{-4}
KBr	2.02	2.02	5.8×10^{-4}
		6.0	4.9×10^{-4}
		10.5	3.1×10^{-4}

In the case of KCl and $Z' = 1.99$ gives an admixture coefficient that agrees quite well with that determined by Hetrick and Compton [15] (4.6×10^{-3}) for the effect of uniaxial stress on the luminescence of the F -center. This would indicate a very diffuse D -state. Our measured values of a -shift in the fourth shell of KBr are smaller than would be expected from this value of scaling parameter. Gourary and Adrian calculate that the $2p$ -state should have a scaling parameter of 5.0,

which means that this wave function has been pulled in over the nearest neighbors. This would indicate that the scaling parameter might be at least this great (5.0) for the still higher energy $3d$ -state. In any case we can quote the value of α for $Z' = 10.5$ as the minimum amount of d -state wave function needed to account for the total observed effect of tetragonal motion (δa_3).

5.5 Second shell ions

If we try to apply equations that do not take into account core distortion to the analysis of the second shell data we find inconsistencies much larger than the experimental error. These discrepancies can be eliminated by use of additional terms that arise from core distortions (amplification factor changes) as was done for the first shell. When this is done the equations become

Stress [100]

$$\delta a_{\perp \text{ meas.}} = \delta a_1 - \delta a_3 + A_3 \quad (25)$$

$$\delta a_{45^\circ \text{ meas.}} = \delta a_1 + \frac{1}{2}\delta a_3 - A'_3. \quad (26)$$

Stress [110]

$$\delta a_{\parallel \text{ meas.}} = \delta a_1 + \frac{1}{2}\delta a_3 + \frac{1}{2}\delta a_5 + \frac{1}{2}A_5 - \frac{1}{2}A_3 \quad (27)$$

$$\delta a_{\perp \text{ meas.}} = \delta a_1 + \frac{1}{2}\delta a_3 - \frac{1}{2}\delta a_5 - \frac{1}{2}A_5 - \frac{1}{2}A_3 \quad (28)$$

$$\delta a_{90^\circ \text{ meas.}} = \delta a_1 - \frac{1}{2}\delta a_3 + X. \quad (29)$$

Stress [111]

$$\delta a_{\perp \text{ meas.}} = \delta a_1 - \delta a_5/3 - A_5/3 - A'_5/3 \quad (30)$$

$$\delta a_{55^\circ \text{ meas.}} = \delta a_1 + \delta a_5/3 + A_5/3 + A'_5/3. \quad (31)$$

The several different correction terms, A_3 , A'_3 , A_5 , A'_5 , X , arise because of the quite different symmetry of the sites in the different stress cases.

Since we have seven unknowns and seven equations there can be no check for internal consistency among the equations. The results of solving these equations with the data of Table 8 are shown in Table 14. Because A_5 always enters the equations with the same

Table 14. Results of computations for second shell KCl (kHz/kg/mm²)

$\delta a_1/(h\delta P)$	-0.6
$\delta a_1/(h\delta P)$ (Liu)	-0.62
$\delta a_3/(h\delta P)$	-0.5
$(\delta a_3 + A_3)/(h\delta P)$	28.5
$A_3'/(h\delta P)$	-6.3
$A_3/(h\delta P)$	3.4
$A_3'/(h\delta P)$	-0.5
$X/(h\delta P)$	1.0

sign as δa_3 the two quite different effects can not be separated. It should be noted that our value of $\delta a_1 = -0.6$ is in excellent agreement with that of Liu[14] who found $\delta a_1 = -0.62$ by hydrostatic pressure techniques. The quantities of Table 14 are expressed as relative frequency shifts per unit of relative bulk strain in Table 15.

Table 15. Relative frequency shifts per unit of relative bulk strain for second shell KCl

Cubic motion	-1.6
Tetragonal mot.	-0.9
Trig. mot. & dist.	3.2
Tet. dist. (A_3)	6.3
Tet. dist. (A_3')	-0.9
Trig. dist. (A_3')	-0.1

The negative a -shift for δa_1 is the most unexpected result in this part of the experiment. Seidel's Rule (equation (19)) is not good for the second shell. In fact there is no good rule for expressing the a -value in terms of the distance from the center of the vacancy for this shell. From a plot of a -value vs. nn distance for the second shell ions one might expect an approximate rule would be $a = K/R^5$. This rule would indicate that the a -shift in the second shell should be 1.7 times more sensitive to cubic distortion than the first shell. The experiment shows that it is about 0.5 times as sensitive and what is still worse the second shell shift has the opposite sign from that of the first shell. This means that one should not think of the a -shift as arising from motion of the ions alone. Stress

must have a very large effect on the F -center wave function.

The larger a -shifts seen for certain classes of second shell ions can be explained in terms of admixture of rhombic wave functions. In fact all of the rhombic type wave functions admixed in by the applied stresses have their lobes pointing toward second shell ions. This explains the low sensitivity of the first shell ion to rhombic, Γ_5 , distortion while the second shell shows a fairly large sensitivity to this distortion. Stress along the [110] axis mixes in a wave function with negative lobes perpendicular to stress and positive lobes along the stress axis. Thus the large position $\delta a_{||}$ and negative $\delta a_{\perp}$ found in this case. Stress along the [111] axis admixes in a Γ_5 wave function which has positive lobes pointing at those ions at 35° to the stress and negative lobes pointing at those ions at 90° to the stress. Again large a -shifts are seen with the correct sign. For those atoms at 35° to stress along [100] and at 60° to stress along [110] there are no admixed wave functions that have lobes pointing in their direction. This explains the very small shift seen for these ions. The D -function, u_{320} , has a negative ring that extends out towards those ions at 90° to stress along [100]. Thus the fairly small negative a -shift seen in this case is expected.

5.6 Fourth shell KBr

This shell has the same symmetry as the first but is composed of negative ions. As data has only been taken along the [110] stress axis, the separation of effects due to different types of distortion is impossible. It should be noted that the average a -shift, $\delta a = -0.5$ agrees quite well with the value $\delta a_1 = -0.43$ found by Liu[14]. This indicates that the other effects (the core distortion corrections as in the first shell data) are quite small in this case.

6. CONCLUSIONS

The observed a -shifts have been explained by using a perturbation Hamiltonian depend-

ing only on the motion of the neighboring nuclei plus a change in the amplification factor due to core distortions of the nuclei. This separation of the two effects gives excellent agreement between our values for the α -shift caused by pure cubic distortion with those found by Liu[14] for pure cubic distortion obtained by means of hydrostatic pressure.

Our upper estimate of the value of the local to bulk compressibility ratio of about one is in disagreement with that obtained from optical work. The interpretation of the optical studies is more complex than the ENDOR results as it depends upon stress effects on two different states. Moreover, the optical transitions will reveal only the average effects depending on all the ions together. There is, however, excellent agreement between our results and those obtained from Raman scattering.

The agreement between our data and that from Raman scattering indicates that Seidel's Rule holds with fair accuracy for the volume changes of the first shell under pressure in KCl and KBr. This rule seems to break down in the case of the Li salts where the smaller upper limit in the local compressibility as obtained from Seidel's Rule is attributed to local lattice relaxation into the vacancy.

Further theoretical work is needed to take full advantage of the detailed experimental stress results and in particular to see if this relaxation of the nearest neighbors can account for the observed hfi in the outer shells. Experiments on crystals with different halogen to alkali ratio size are needed to confirm the above predictions. For example it would be useful to see if KF (ratio of ion size ≈ 1) does not show a larger sensitivity to cubic

distortions than any of the samples studied here.

Acknowledgement—It is a pleasure to thank Professor W. T. Doyle, my thesis advisor, for suggesting the experiment and for many stimulating discussions during the course of the work.

REFERENCES

1. See for example: SCHULMAN J. H. and COMPTON W. D., *Color Centers in Solids*, Macmillan Press, New York (1962); MARKHAM J., *Solid State Physics*, Supp. 8, Academic Press, New York (1966).
2. JACOBS I. S., *Phys. Rev.* **93**, 993 (1954).
3. GEBHARDT W. and MAIER K., *Phys. Status Solidi* **8**, 303 (1965).
4. SCHNATTERLY S. E., *Phys. Rev.* **140**, A1364 (1965).
5. ABRAGAM A., *The Principles of Nuclear Magnetism*, Oxford University Press, London (1962).
6. SEIDEL H., *Z. Phys.* **165**, 218 (1961).
7. GOURARY B. S. and ADRIAN F. J., *Phys. Rev.* **105**, 1180 (1957).
8. BAILEY C. E., thesis, Dartmouth College, 1968 (unpublished).
9. SCHAWLOW A. L., PIKSIS A. H. and SUGANO S., *Phys. Rev.* **122**, 1469 (1961).
10. We have used the notation of BETHE H. A., *Annln. Phys.* **3**, 133 (1929).
11. FEHER G., *Phys. Rev.* **105**, 1122 (1957).
12. DOYLE W. T., *Phys. Rev.* **126**, 1421 (1962).
13. DOYLE W. T., *Rev. scient. Instrum.* **33**, 118 (1962).
14. LIU H. P., thesis, Dartmouth College, 1968 (unpublished).
15. HETRICK R. E. and COMPTON W. D., *Phys. Rev.* **155**, 649 (1967).
16. DOYLE W. T., (private communication).
17. FEUCHTWANG T. E., *Phys. Rev.* **126**, 1616 1628 (1962).
18. DAVITASHVILI T. SH. and POLITOV N. G., *Soviet Phys. solid St.* **8**, 1948 (1967).
19. IVEY H. F., *Phys. Rev.* **72**, 341 (1947).
20. BUCHENAUER C. J. and FITCHEN D. B., *Phys. Rev.* **167**, 846 (1968).
21. BLUM H., *Phys. Rev.* **140**, A1998 (1965).
22. BENEDEK G. and NARDELLI G. F., *Phys. Rev.* **154**, 872 (1967).
23. BENEDEK G. and NARDELLI G. F., *Phys. Rev.* **167**, 837 (1968).

CONTRIBUTION TO THE THEORY OF KONDO RESISTIVITY IN MAGNETIC COMPOUNDS

F. E. MARANZANA

Philips Research Laboratories, N.V. Philips' Gloeilampenfabrieken, Eindhoven, Netherlands

(Received 15 October 1969; in revised form 8 December 1969)

Abstract—The theory of Kondo exchange scattering has been extended to the case in which the scattering system consists of a periodic spin structure.

1. INTRODUCTION

THE FOLLOWING pages contain a variation of Kondo's original calculation[1] of the resistivity of dilute magnetic alloys. The present calculation applies rather to systems in which the magnetic ions make up a large percentage of the total number of atoms present in the system. Moreover the magnetic ions are arranged periodically so that the results to be obtained are not to be applied to alloys containing large concentrations of magnetic impurities. One should rather compare the present results to the experimental evidence available on the intermetallic compound CeAl_2 [2].

The experimental situation in the case of CeAl_2 is briefly summarized as follows: the resistivity vs. temperature curve has a maximum approximately at the ordering temperature (as determined by magnetic susceptibility measurements), then it decreases for increasing temperatures, it has a clear minimum, and it increases further. The minimum has been thought to be indicative of the presence of the Kondo effect[2]. Further, the partial substitution of Th for Ce influences the resistivity curve: with increasing Th percentages the maximum and the minimum become vaguer, and they finally disappear. For this Th concentration the resistivity versus temperature curve rises rapidly up to the transition temperature, it shows a plateau, and then starts rising again.

The effects of the Th substitution have been

interpreted[2] by suggesting that the density of states of the system's conduction band is diminished by the addition of Th. The results obtained on systems containing Th in place of Ce have been put forward as further support of the presence of Kondo anomalies, in view of the relevance of the density of states in the formulae applying to the Kondo effect in dilute alloys.

The formula to be derived at present reproduces rather nicely the experimental evidence; this is not really surprising, if one recalls that the essential features to be obtained (a density-of-states dependent minimum in the resistivity vs. temperature curve), are already present in the dilute alloy calculation. It is on the other hand pleasant that a Kondo-like formula can be constructed for a system containing many magnetic ions, so that the possibility of the presence of the Kondo effect in a concentrated system gains further credibility. There exist in fact theoretical studies on concentrated magnetic alloys[3] which predict that when the concentration of the magnetic ions is larger approximately than 1 per cent and there exists no long-range magnetic order, the minimum disappears. The point of the present calculation is that this is not true when the magnetic ion system consists of a periodic spin lattice, in which long-range order exists. Abrikosov[4] has considered the case of a concentrated alloy in which long-range order exists. The results of this author apply to a model which differs essentially from the

present one. Abrikosov places in fact the magnetic ions on a number of randomly selected lattice sites.

The present calculation is imitated step by step from Kondo's [1]. It will consequently be described very briefly.

2. DESCRIPTION OF THE MODEL AND OF THE CALCULATION

N magnetic ions are arranged on a simple cubic lattice in a crystal of volume V . The spins of the ions interact with one another through a Heisenberg interaction. The Heisenberg interaction is taken into account in the following by means of a molecular field: each spin is supposed to move in the presence of this temperature dependent field, and it moves otherwise independently of the other spins. Conventional molecular field theory is adopted, so that, for instance, the average length of each spin is determined by the usual implicit equation containing on the right-hand side a Brillouin function whose argument is again a function of the average length of the spin.

The conduction of the system is accounted for by a Fermi sea of electrons residing in a band extending from $-E_1$ to E_2 with a constant density of states $n(E_F)$. The Fermi level is taken as the zero of energy so that $E_F = 0$. The interaction of the 'conduction system' and the 'magnetic system' amounts to the usual s - f interaction:

$$\mathcal{H}' = -\frac{J}{N} \sum_{kk'n} e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_n} \times [(a_{k'\uparrow}^\dagger a_{k\uparrow} - a_{k'\downarrow}^\dagger a_{k\downarrow}) S_n z + a_{k'\uparrow}^\dagger a_{k\downarrow} S_n^- + a_{k'\downarrow}^\dagger a_{k\uparrow} S_n^+]. \quad (1)$$

(Strictly speaking, one should derive the RKKY part of the Heisenberg interaction from the s - f interaction.) The calculation runs along the following lines: the transition probability up to third order in J is calculated. Only elastic scattering is considered, so that processes of the type $\mathbf{k}\uparrow \rightarrow \mathbf{k}'\downarrow$ are neglected,

on the basis of the fact that they probably contribute terms of the same order of magnitude and temperature dependence as the terms retained, and these can therefore be considered representative of the general behaviour. (Notice that the procedure followed does not exclude, in second order, processes of the type $\mathbf{k}\uparrow \rightarrow \mathbf{k}'\downarrow \rightarrow \mathbf{k}'\uparrow$ and the typical Kondo-like processes). The transition probability terms proportional to J^2 and J^3 are given by the formulae:

$$W_1(\alpha', \alpha) = \frac{2\pi}{\hbar} \delta(E_\alpha - E_{\alpha'}) |\langle \alpha' | \mathcal{H}' | \alpha \rangle|^2 \quad (2)$$

$$W_2(\alpha', \alpha) = \frac{2\pi}{\hbar} \delta(E_\alpha - E_{\alpha'}) \left\{ \langle \alpha' | \mathcal{H}' | \alpha \rangle \times \sum_{\alpha''} \left[\frac{\langle \alpha | \mathcal{H}' | \alpha'' \rangle \langle \alpha'' | \mathcal{H}' | \alpha' \rangle}{E_\alpha - E_{\alpha''} + i\eta} + \text{c.c.} \right] \right\}. \quad (3)$$

The ket $|\alpha\rangle$ represents a state which is labelled by the $\mathbf{k}$ vectors and the spins σ of all conduction electrons, and by the magnetic quantum numbers of all magnetic ions. Substitution of (1) into (2) gives:

$$\begin{aligned} W_1(k'\uparrow, k\uparrow) &= W_1(k'\downarrow, k\downarrow) \\ &= \frac{2\pi}{\hbar} \delta(E_k - E_{k'}) \\ &\times \left[-\frac{J}{N} \right]^2 \sum_{nn'} m_n m_{n'} \\ &\times \exp[i(\mathbf{k} - \mathbf{k}') \cdot (\mathbf{R}_n - \mathbf{R}_{n'})]. \end{aligned} \quad (4)$$

The transition probability term proportional to J^3 is different for the two orientations of the spin of the electron being scattered from $\mathbf{k}$ to $\mathbf{k}'$. Moreover for either spin direction four different intermediate states are possible involving the scattering of either one or two electrons in typical Kondo-like processes. Substitution of (1) into (3) gives:

$$\begin{aligned}
& \pm \left(-\frac{J}{N}\right)^3 \sum_{lmn, k''} m_l m_m m_n \\
& \times \exp [i\{(k-k')R_l + (k''-k)R_m \\
& + (k'-k'')R_n\}] \left[\frac{1-f_{k''}}{E_k - E_{k''} + i\eta} + \text{c.c.} \right] + \\
& \pm \left(-\frac{J}{N}\right)^3 \sum_{lmn, k''} m_l [S(S+1) - m_m(m_m \pm 1)] \\
& \times \exp [i\{(k-k')R_l + (k'-k)R_m\}] \\
& \times \left[\frac{1-f_{k''}}{E_k - E_{k''} + i\eta} + \text{c.c.} \right] + \\
& \mp \left(-\frac{J}{N}\right)^3 \sum_{lmn, k''} m_l m_m m_n \\
& \times \exp [i\{(k-k')R_l + (k''-k)R_m + (k'-k'')R_n\}] \\
& \times \left[\frac{f_{k''}}{-E_k + E_{k''} + i\eta} + \text{c.c.} \right] + \\
& \mp \left(-\frac{J}{N}\right)^3 \sum_{lmn, k''} m_l [S(S+1) - m_m(m_m \mp 1)] \\
& \times \exp [i\{(k-k')R_l + (k'-k)R_m\}] \\
& \times \left[\frac{f_{k''}}{-E_k + E_{k''} + i\eta} + \text{c.c.} \right].
\end{aligned} \tag{5}$$

The upper sign applies to the scattering of an electron with spin up, the lower sign applies to the scattering of an electron with spin down. The transition probability contains factors of the type

$$\sum_{l, r, n} m_l m_r m_n \exp \{i[(\mathbf{k}-\mathbf{k}')\mathbf{R}_l + (\mathbf{k}''-\mathbf{k})\mathbf{R}_r + (\mathbf{k}'-\mathbf{k}'')\mathbf{R}_n]\} \tag{6}$$

$$\sum_{ln} m_l [S(S+1) - m_n(m_n - 1)] \times \exp \{i[(\mathbf{k}-\mathbf{k}')\mathbf{R}_l + (\mathbf{k}'-\mathbf{k})\mathbf{R}_n]\} \tag{7}$$

where m_l is the azimuthal quantum number of the l -th spin, $(S(S+1))^{1/2}$ is the length of the spins.

These factors are averaged by Kondo on the assumption that no internal field is present: the magnetic impurities are so dilute that they 'do not see one another'. In the case under consideration the process of averaging proceeds as follows: in the case of

$$\sum_{ln} m_l m_n \exp \{i[(\mathbf{k}-\mathbf{k}')\mathbf{R}_l + (\mathbf{k}'-\mathbf{k})\mathbf{R}_n]\} \tag{8}$$

for example,

$$\begin{aligned}
& \left\langle \sum_{ln} m_l m_n \exp \{i[(\mathbf{k}-\mathbf{k}')\mathbf{R}_l + (\mathbf{k}'-\mathbf{k})\mathbf{R}_n]\} \right\rangle = \sum_{ln} \langle m_l m_n \rangle \\
& \times \exp \{i[(\mathbf{k}-\mathbf{k}')\mathbf{R}_l + (\mathbf{k}'-\mathbf{k})\mathbf{R}_n]\} \\
& = N \langle m^2 \rangle + \langle m \rangle^2 \sum_{n \neq l} 1 \\
& \times \exp \{i[(\mathbf{k}-\mathbf{k}')\mathbf{R}_l + (\mathbf{k}'-\mathbf{k})\mathbf{R}_n]\} \\
& = N \langle m^2 \rangle + \langle m \rangle^2 \\
& \times \{-N + \text{terms containing } \delta(\mathbf{k}-\mathbf{k}')\} \\
& = N \langle (m - \langle m \rangle)^2 \rangle + \text{terms containing } \delta.
\end{aligned}$$

In this calculation the periodicity of the magnetic system plays an essential role, because it allows one to split the term of equation (4) into a k -independent term and a contribution of the electron's self-energy which is of no interest for the scattering. It is interesting to consider the effects of two types of deviation from periodicity, namely the case of a concentrated alloy in which the magnetic ions are placed at random in the matrix, and the case of a periodic spin structure in which some of the magnetic ions are replaced by non-magnetic ones.

In the case of the concentrated alloy (treated in ref. [4] by a different technique) the positions $\mathbf{R}_n$ of the magnetic ions are distributed at random. This has as a consequence that $\sum_n \exp [i\mathbf{k}\mathbf{R}_n]$ is equal to a delta function plus other terms dependent upon $\mathbf{k}$. The form of these terms depends upon the distribution

of the magnetic ions and it is extremely difficult to compute in practice. In the case of the replacement of a small fraction of magnetic ions by non-magnetic ones, the results obtained above are not significantly modified. γN terms appear besides $N\langle(m - \langle m \rangle)^2\rangle$ but they do not contain N , and can be neglected as long as $\gamma \ll 1$. When the above described averages are performed on W_1 and W_2 one obtains:

$$\begin{aligned} W_1(k' \uparrow, k \uparrow) &= W_1(k' \downarrow, k \downarrow) \\ &= \frac{2\pi}{\hbar} \delta(E_k - E_{k'}) \\ &\quad \times \left(\frac{J}{N}\right)^2 N\langle(m - \langle m \rangle)^2\rangle \\ W_2(k' \uparrow, k \downarrow) &= \frac{2\pi}{\hbar} \delta(E_k - E_{k'}) \\ &\quad \times \left[-2\left(-\frac{J}{N}\right)^3 N\langle(m - \langle m \rangle)^2\rangle\right. \\ &\quad \times (1 \pm 2\langle m \rangle) \sum_{k''} \frac{1}{E_k - E_{k''}} \\ &\quad + 4\left(-\frac{J}{N}\right)^3 N\langle(m - \langle m \rangle)^2\rangle \\ &\quad \left. \times \sum_{k''} \frac{f_{k''}}{E_k - E_{k''}}\right]. \end{aligned}$$

The relaxation time is obtained in the conventional way by summing over k' : A spin independent relaxation time is obtained by summing the relaxation times proper to electrons with spin up and down. This relaxation time is introduced in the well-known formula for the conductivity and the result for the resistivity is finally obtained:

$$\begin{aligned} \rho &= \frac{3\pi}{2} \frac{1}{\hbar e^2} \frac{V}{N} \frac{J^2}{v_F^2} \langle(m - \langle m \rangle)^2\rangle \\ &\quad \times \left[1 + \frac{2Jn(E_F)}{N} \left\{ \ln \left| \frac{E_1}{E_2} \right| - 2 \ln \left| \frac{E_1}{kT} \right| \right\} \right] \quad (9) \end{aligned}$$

where v_F is the Fermi velocity.

3. DISCUSSION

Inspection of equation (9) shows the following: the factor outside the square bracket corresponds to usual spin-disorder scattering in the elastic approximation. Its temperature dependence is such that the resistivity increases rapidly up to the transition temperature and thenceforth remains constant. In the case under consideration this factor is corrected by the square bracket. This bracket contains a temperature-independent correction and the Kondo logarithmic term. The former correction is temperature independent owing to the rough way in which the sums over k and k' have been performed to obtain the relaxation time and the conductivity. This correction is anyway some four times smaller than the second one, because E_1 is presumably of the same order of magnitude as E_2 while kT is approximately 10^4 times smaller. The sign of the former correction depends upon the relative magnitude of E_1 and E_2 . The latter correction is positive if J is negative and it represents the essential part of the correction to spin-disorder scattering. Below the transition temperature the temperature dependence of this correction is overridden by the T dependence of spin-disorder resistivity, but it appears on the contrary above the transition temperature; in this temperature region the total resistivity then decreases with increasing temperature. The maximum at the transition temperature shown by the experimental resistivity is thus reproduced. The minimum above the transition temperature is obtained, as usual, by adding to this resistivity an increasing term due to phonon scattering. It is also evident from equation (9) that the density of states $n(E_F)$ plays a decisive role in producing the extrema in the resistivity curve. The extrema are washed out if the density of states decreases. Then normal spin-disorder scattering remains.

In essence equation (9) describes the following state of affairs: below the transition temperature an internal field acts on each magnetic ion's spin and it prevents it from flipping. If

spin flip is forbidden the Kondo scattering processes do not take place and the $\ln T$ term is quenched. At the transition temperature however the internal field drops to zero. Then above this temperature each magnetic ion is free to flip its spin under the influence of the s - f interaction and this gives rise to the $\ln T$ term.

Figure 1 shows a plot of resistivity vs. temperature as derived numerically from equation (9). The calculation of $\langle (m - \langle m \rangle)^2 \rangle$ has been performed by assuming that the magnetic ions have total angular momentum equal to $\frac{5}{2}$, like cerium ions. Each ion has six energy levels labelled by the value of the azimuthal quantum number m . The levels are degenerate in the absence of fields. In the present case

however the ions are under the influence of a cubic crystal field and the internal molecular field proportional to $z g \Gamma$, where z is the number of nearest neighbouring magnetic ions, g is the Landé factor, and Γ is the Heisenberg coupling constant. If the internal field is absent, as in the paramagnetic region, the crystal field splits the sextet into a doublet and a quartet (5). It has been assumed for the calculation that the doublet is the ground state, the quartet being separated from the doublet by a distance of 80°K .

This assumption seems to be contradicted by preliminary experimental indications (6) that suggest that the quartet is the ground state. However, the reversal of the sign of the crystal field would not change the general behaviour of spin-disorder resistivity. Also, these considerations on the internal structure of the magnetic ions have minor relevance with respect to the influence of the Kondo terms. The presence of the internal field splits the doublet and the quartet further. The magnetic transition temperature is such ($\approx 10^\circ\text{K}$) that the internal field can be looked upon as a small correction to the crystal field.

Within this model the relevant quantity

$$\langle (m - \langle m \rangle)^2 \rangle = \langle m^2 \rangle - \langle m \rangle^2 \quad (10)$$

is obtained through the equation

$$\langle m^n \rangle = \text{Spur} (m_z^n \mathcal{H}) \quad n = 1, 2 \quad (11)$$

where H is the sum of the internal field $z g \Gamma \langle m \rangle$ plus crystal field hamiltonians m_z is the z component of the spin operator S of one of the magnetic ions. The following parameters have been used in the numerical calculations: $\ln |E_1/E_2| = 1$; $E_1 = 5 \text{ eV}$; $z g \Gamma = 7^\circ\text{K}$; the curves of Fig. 1 give the behaviour of the resistivity vs. temperature. The variable on the ordinate axis is ρ divided by the numerical factors appearing on the right-hand side of equation (9). The different curves have been obtained by attributing to the parameter $2J_n(E_F)/N$ the values reported in the figure.

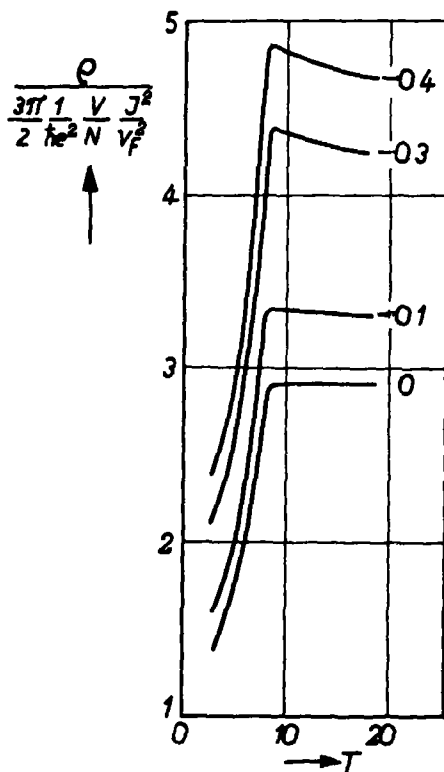


Fig. 1. Resistivity vs. temperature curve obtained from equation (9) in the text. Each curve is labelled by the corresponding value of the parameter $2J_n(E_F)/N$.

A comparison of Fig. 1 with the experimental curves (2) shows that the agreement is quite satisfactory. In this respect however a word of caution is in order. The theory assumes that the density of states can be changed without modifying the magnetic ion system. In practice the substitution of thorium for cerium breaks up the translational symmetry of the magnetic ion system, making the application of the theory doubtful at least at large Th concentrations. Also, the fact that the number of Ce ions decreases changes the transition temperature experimentally. The theory does not take this effect into account. Finally of course one should be suspicious of a calculation based on perturbation theory and the molecular field theory.

Acknowledgements—The author is grateful to Dr. H. J. van Daal and Dr. K. H. J. Buschow for a number of fruitful discussions.

REFERENCES

1. KONDO J., *Prog. theor. Phys.* **32**, 37 (1964).
2. BUSCHOW K. H. J. and VAN DAAL H. J., *Phys. Rev. Lett.* **23**, 408 (1969).
3. HARRISON R. J. and KLEIN M. W., *Phys. Rev.* **154**, 540 (1967).
4. ABRIKOSOV A. A., *Physics* **2**, 61 (1965).
5. LEA K. R., LEASK M. J. M., and WOLF W. P., *J. Phys. Chem. Solids* **23**, 1381 (1962).
6. WALLACE W. E., CRAIG R. S., THOMPSON A., DEENADAS C., DIXON M., AOYAGI M., and MARZOUK M., *Proc. du Colloque International sur les Elements des Terres Rares*. Paris-Grenoble 5-10 May (1969); to be published. See however HILL R. W. and MACHADO da SILVA J. M., *Phys. Lett.* **30A**, 13 (1969).

STRUCTURES MAGNETIQUES ANISOTROPES DANS LES SPINELLES*

B. BOUCHER, R. BUHL† et M. PERRIN†

Service de Physique du Solide et de Résonance Magnétique, Centre d'Etudes Nucléaires de Saclay, BP n° 2, 91, Gif-sur-Yvette, France

(Received 21 November 1969)

Résumé—On développe une théorie de champ moléculaire afin de déterminer les configurations de moments magnétiques énergétiquement stables en présence d'anisotropie dans les spinelles cubiques et quadratiques.

Les hypothèses de base sont: dans un spinelle normal contenant des ions magnétiques dans les sous-réseaux *A* et *B*, les interactions *A*–*B* sont prédominantes et anisotropes. Les moments *A* sont ordonnés ferromagnétiquement et n'ont pas d'anisotropie, seuls les moments *B* possèdent une anisotropie locale. La maille magnétique reste soit cubique faces centrées soit quadratique centrée. Le

$$\mathcal{H} = - \sum_k [\mu_B \mathbf{H}_A [G^k] S_{Bk} + \mu_B \mathbf{H}_0 [g^k] S_{Bk}] - \mu_B \mathbf{H}_0 \cdot \mathbf{S}_A$$

où $\mathbf{H}_A$ est le champ créé par l'ensemble des spins $\mathbf{S}_A$, $\mathbf{H}_0$ le champ extérieur, $[g^k]$ et $[G^k]$ sont les tenseurs représentant les anisotropies locale et d'échange relatives à l'ion B_k , ils ont même symétrie que l'octaèdre d'oxygène. En minimisant l'énergie la plus basse, on trouve à 0°K et champ extérieur nul une solution générale correspondant à une configuration non régulière des moments *B*. Les moments résultants des sous-réseaux *A* et *B* ne sont en général pas colinéaires. On décrit quelques cas particuliers de structures magnétiques possibles suivant des directions cristallographiques simples.

L'évolution de quelques unes de ces configurations en présence d'un champ magnétique extérieur est décrite et, fait apparaître des propriétés spécifiques aux structures anisotropes. Ces propriétés ont été trouvées expérimentalement sur quelques manganites spinelles.

Abstract—A molecular field theory is developed to find the magnetic moment configurations which are energetically stable when anisotropy is present in cubic and tetragonally distorted spinels.

The starting assumptions are: in a normal spinel having magnetic ions in both *A* and *B* sublattices, *A*–*B* interactions are predominant and anisotropic. *A* moments are ferromagnetically ordered and have no anisotropy, only *B* moments have a local anisotropy. The magnetic cells remain either fc for the cubic or bc for the tetragonal spinels. The general Hamiltonian for the whole system of magnet-sublattices is:

$$\mathcal{H} = - \sum_k [\mu_B \mathbf{H}_A [G^k] S_{Bk} + \mu_B \mathbf{H}_0 [g^k] S_{Bk}] - \mu_B \mathbf{H}_0 \cdot \mathbf{S}_A$$

where $\mathbf{H}_A$ is the field created by $\mathbf{S}_A$ spins, $\mathbf{H}_0$ the external field, $[G^k]$ and $[g^k]$ are the tensors representing exchange and local anisotropy for the B_k ion, they have the same symmetry as the surrounding oxygen octahedron. By minimizing the lowest energy we find at 0°K and zero external field a general solution corresponding to a non regular configuration of *B* moments. The resulting moments of *A* and *B* sublattices are generally not collinear. Some particular cases of possible magnetic structures along simple crystallographic directions are described.

The evolution of some of these configurations when an external magnetic field is applied, is described and this shows the specific behaviour of anisotropic structures. These properties have been found experimentally in some spinel manganites.

*Cet article recouvre une partie de la thèse de Doctorat d'état de R. Buhl soutenue le 2 Juin 1969 à Paris (N° CNRS: AO3314).

†Laboratoire de Magnétisme, Département de Recherches Physiques Faculté des Sciences, 11, Quai St Bernard, 75 Paris(5e) France.

1. INTRODUCTION

IL EST remarquable de constater que toutes les théories classiques permettant de définir les structures magnétiques possibles soient basées uniquement sur des considérations

d'échange isotrope (ferrimagnétisme de Néel [1], de Yafet et Kittel [2], structure en 'étoile' [3] ou héliamagnétisme [4]). L'anisotropie ne joue alors que le rôle d'une perturbation venant soit déterminer la direction de facile aimantation dans le cristal soit faire dévier légèrement les moments par rapport à un antiferromagnétisme rigoureux comme dans le cas de NiF_2 traité par Moriya [5]. La plupart des composés de la série des manganites spinelles de formule MeMn_2O_4 possèdent une très forte anisotropie (par exemple $\text{Me} = \text{Co}$ [6], Cr [7], Fe [8] ou Mn [9]). Leurs structures magnétiques ne sont pas simples et certaines de leurs propriétés obligent à penser que l'anisotropie a un rôle déterminant dans la stabilité et la configuration des motifs magnétiques dans le cristal. Nous développons donc ici une théorie de champ moléculaire faisant intervenir les anisotropies locale et d'échange comme facteurs de base pour la détermination des structures magnétiques possibles dans les spinelles cubiques et quadratiques.

2. GENERALITES ET HYPOTHESES DE BASE

Nous ne considérerons ici que les spinelles dont la maille magnétique reste à 0°K cubique faces centrées ou quadratique centrée. Il n'existe donc que deux sous-réseaux magnétiques A : M_1 et M_2 (sites tétraédriques) et quatre B : M_3 , M_4 , M_5 et M_6 (sites octaédriques).

Dans un spinelle cubique ou quadratique contenant des ions magnétiques dans chaque sous-réseau, on fait les hypothèses suivantes:

(1) Les sites tétraédriques A sont occupés par une sorte d'ion dont les moments sont ordonnés ferromagnétiquement et ne possèdent pas d'anisotropie locale.

(2) Les sites octaédriques B sont occupés par une autre sorte d'ion dont les moments possèdent une anisotropie locale.

(3) Les interactions d'échange prédominantes sont les interactions $A-B$, elles sont anisotropes. (Il faut noter que l'introduction d'interactions $B-B$ isotropes ne modifie pas

qualitativement les résultats et pour simplifier les calculs, elles seront donc négligées).

Dans ces conditions, l'énergie d'interaction entre un moment magnétique B_k (de spin S_{B_k}) et la champ H_A créé par l'ensemble des spins du sous-réseau A est:

$$-\mu_B H_A [G^k] S_{B_k} \quad (1)$$

H_A est proportionnel à S_A et $[G^k]$ est le tenseur représentant l'anisotropie d'échange $A-B$ et relatif à l'ion B_k .

En présence d'un champ extérieur H_0 , le Hamiltonien de l'ensemble des sous-réseaux magnétiques s'écrit:

$$\mathcal{H} = - \sum_k [\mu_B H_A [G^k] S_{B_k}^k + \mu_B H_0 [g^k] S_{B_k}^k] - \mu_B H_0 \cdot S_A \quad (2)$$

$[g^k]$ étant le tenseur d'anisotropie locale d'un ion B_k .

L'énergie minimum par rapport aux spins S_B et exprimée en fonction des composantes sur les trois axes est:

$$E = -\mu_B \sum_k S_B \sqrt{\sum_j \left[(H_A' G_{jk}^k + H_0' g_{jk}^k) \right]^2} - \mu_B \sum_j H_0' S_A^j \quad (3)$$

Soit lorsque le champ extérieur est nul:

$$E = -\mu_B S_B \sum_k \sqrt{\sum_j \left[H_A' G_{jk}^k \right]^2} \quad (4)$$

En minimisant cette énergie par rapport à H_A il est donc possible de déterminer à 0°K et à champ nul les solutions possibles pour H_A puis de calculer les moments M_B et ainsi de définir complètement les configurations magnétiques possibles.

Dans le cas des spinelles, l'octaèdre d'oxygène entourant un ion B n'a pas la symétrie idéale $O_h(4/m\bar{3}2/m)$ mais il est déformé et ne possède plus qu'une symétrie trigonale $D_{3d}(\bar{3}m)$ dans le groupe d'espace cubique $O_h(Fd\bar{3}m)$, ou monoclinique

$C_{2h}(2/m)$ dans le groupe quadratique $D_{4h}^{19}(14_1/2md)$. Connaissant la symétrie du site, il est possible de déterminer la forme des tenseurs G et g qui ont mêmes axes. La forme la plus générale correspond évidemment à la symétrie la plus faible, c'est-à-dire ici à C_{2h} dans le cas du spinelle quadratique.

Spinelle quadratique

En prenant pour axes de référence de l'octaèdre: l'axe binaire: Ox correspondant d'ailleurs à la direction $[100]$ de la maille, les deux autres axes sont contenus dans le miroir m et sont pris de la manière suivante: Oy parallèle à la direction $[010]$ et Oz parallèle à la direction $[001]$.

En appliquant au tenseur le plus général (9 composantes non nulles) les opérations de symétrie de l'octaèdre, il apparaît des simplifications qui conduisent au tenseur représentant l'anisotropie dans un octaèdre de symétrie $2/m$:

$$[g] = \begin{bmatrix} g_{11} & 0 & 0 \\ 0 & g_{22} & g_{23} \\ 0 & g_{32} & g_{33} \end{bmatrix}$$

$[G]$ a la même forme.

Spinelle cubique

L'octaèdre ayant une symétrie plus élevée: $\bar{3}m$, la forme du tenseur d'anisotropie doit être plus simple. Prenons en effet comme axes de référence:

Ox : l'axe binaire perpendiculaire au miroir contenant l'axe $\bar{3}$
 Oy : l'axe $\bar{3}$
 et Oz : l'axe perpendiculaire aux deux premiers.

En appliquant les opérations de symétrie on est conduit au tenseur représentant l'anisotropie dans un octaèdre de symétrie $\bar{3}m$:

$$[g] = \begin{bmatrix} g_{11} & 0 & 0 \\ 0 & g_{22} & 0 \\ 0 & 0 & g_{11} \end{bmatrix}$$

$[g]$ a donc une forme extrêmement simple dans ce système d'axes propres à l'octaèdre. Les opérations de symétrie de la maille cubique faisant passer d'un octaèdre à l'autre ne sont malheureusement pas décrites dans ce système de référence. Il est donc nécessaire d'effectuer un changement d'axes de l'octaèdre afin de décrire son anisotropie dans un système commun à celui de la maille. Au lieu de prendre comme axes de référence trois directions de la forme $[100]$, il est plus avantageux de prendre les axes: Ox parallèle à la direction $[1\bar{1}0]$, Oy // $[110]$ et Oz // $[001]$. (Ces axes dans le système cubique faces centrées correspondent à ceux que nous avons pris pour le système quadratique centré).

Dans ce système de référence le tenseur $[g]$ devient:

$$[g] = \begin{bmatrix} g_{11} & 0 & 0 \\ 0 & \frac{1}{3}(2g_{22} + g_{11}) & \frac{\sqrt{2}}{3}(g_{22} - g_{11}) \\ 0 & \frac{\sqrt{2}}{3}(g_{22} - g_{11}) & \frac{1}{3}(g_{22} + 2g_{11}) \end{bmatrix}$$

ce tenseur a exactement la même forme que celui déterminé pour les spinelles quadratiques, seules des relations entre les composantes en réduisent la généralité.

En conclusion, il suffira de traiter en détail le cas des spinelles quadratiques puis de voir si les particularités du système cubique entraînent des modifications aux résultats.

3. STRUCTURES MAGNETIQUES ANISOTROPES POSSIBLES A 0°K ET A CHAMP NUL

(3.1) Cas général

(3.1.1) *Spinelles quadratiques.* Les ions B_k porteurs des moments M_3, M_4 etc... sont définis par leur position dans la maille du groupe D_{4h}^{19} (origine à $\bar{4}m2$) $B_3(0, \frac{1}{4}, \frac{1}{4})$; $B_4(0, \frac{3}{4}, \frac{1}{4})$; $B_5(\frac{1}{4}, 0, \frac{1}{4})$ et $B_6(\frac{3}{4}, 0, \frac{1}{4})$.

En tenant compte de la symétrie quadratique de la maille et en l'absence de champ magnétique extérieur, l'énergie s'écrit:

$$E = -\mu_B S \left\{ \begin{aligned} & \sqrt{G_{11}^2 H_x^2 + (G_{22} H_y + G_{23} H_z)^2 + (G_{32} H_y + G_{33} H_z)^2} \\ & + \sqrt{G_{11}^2 H_x^2 + (G_{22} H_y - G_{23} H_z)^2 + (-G_{32} H_y + G_{33} H_z)^2} \\ & + \sqrt{G_{11}^2 H_y^2 + (G_{22} H_x - G_{23} H_z)^2 + (-G_{32} H_x + G_{33} H_z)^2} \\ & + \sqrt{G_{11}^2 H_y^2 + (G_{22} H_x + G_{23} H_z)^2 + (G_{32} H_x + G_{33} H_z)^2} \end{aligned} \right\}. \quad (5)$$

Pour déterminer la direction stable de H_A , il suffit donc de minimiser cette énergie. En tenant compte du fait que $H_A^2 = \sum_i (H_A^i)^2$ on obtient:

$$\begin{aligned} \frac{\partial E}{\partial H_x} = & \left[(G_{11}^2 - G_{23}^2 - G_{33}^2) \left(\frac{1}{\alpha} + \frac{1}{\beta} \right) \right. \\ & + (G_{22}^2 + G_{32}^2 - G_{23}^2 - G_{33}^2) \left(\frac{1}{\gamma} + \frac{1}{\delta} \right) \left. \right] H_x \\ & - (G_{22} G_{23} + G_{32} G_{33}) \left(\frac{1}{\alpha} - \frac{1}{\beta} \right) \frac{H_x H_y}{H_z} \\ & + (G_{22} G_{23} + G_{32} G_{33}) \left(\frac{1}{\delta} - \frac{1}{\gamma} \right) \\ & \times \left(H_z - \frac{H_x^2}{H_z} \right) \end{aligned} \quad (6)$$

$\partial E / \partial H_y$ a exactement la même forme, il suffit de permuter H_x et H_y . α, β, γ et δ sont respectivement les quatre racines carrées contenues dans l'expression de l'énergie (équation (5)).

Les conditions nécessaires $\partial E / \partial H_x$ et $\partial E / \partial H_y = 0$ ne sont pas des relations simples et il existe a priori, une solution générale où H_x , H_y et H_z sont tous différents de zéro. On voit donc que pour un système de G_{ij} et g_{ij} donné, il existe une configuration magnétique dont l'énergie est donnée par l'équation (5) en remplaçant H_x , H_y et H_z par les valeurs qui annulent $\partial E / \partial H_y$ (équation (6)).

Supposons donc stable une telle solution générale définie par les composantes H_A^i et, cherchons à déterminer la configuration

correspondante des moments des ions B afin de décrire complètement la structure magnétique.

On peut déterminer les composantes des moments M_B en écrivant:

$$M_{Bk} = \sum_j g_{Bj}^k S_{Bj}^k$$

(ce qui oblige à calculer les composantes des spins) ou bien, ce qui revient au même, en dérivant directement l'expression de l'énergie d'un ion B par rapport au champ extérieur.

L'énergie d'un ion B est:

$$E_k = -\mu_B S_B \sqrt{\sum_j \left[\sum_i (H_A^i G_{ji}^k + H_0^i g_{ji}^k) \right]^2}. \quad (7)$$

Les constantes d'un moment M_k sont:

$$\begin{aligned} M_{Bk}^i &= \frac{-\partial E_k}{\partial H_0^i} \\ &= \frac{\sum_j g_{Bj}^k \left[\sum_i (H_A^i G_{ji}^k + H_0^i g_{ji}^k) \right]}{\sqrt{\sum_j \left[\sum_i (H_A^i G_{ji}^k + H_0^i g_{ji}^k) \right]^2}} \mu_B S_B. \end{aligned} \quad (8)$$

Soit lorsque le champ extérieur est nul:

$$M_{Bk}^i = \frac{\sum_j g_{Bj}^k \left(\sum_i G_{ji}^k H_A^i \right)}{\sqrt{\sum_j \left(\sum_i G_{ji}^k H_A^i \right)^2}} \mu_B S_B. \quad (9)$$

Nous pouvons donc écrire par exemple les composantes du moment de l'atome B_3 à champ extérieur nul et dans le cas d'une solution générale:

$$M_{3x} = \frac{g_{11} G_{11} H_x}{\sqrt{G_{11}^2 H_x^2 + (G_{22} H_y + G_{23} H_z)^2 + (G_{32} H_y + G_{33} H_z)^2}} \mu_B S_B. \quad (10)$$

$$M_3^y = \frac{g_{22}(G_{22}H_y + G_{23}H_z) + g_{23}(G_{32}H_y + G_{33}H_z)}{\sqrt{G_{11}^2H_x^2 + (G_{22}H_y + G_{23}H_z)^2 + (G_{32}H_y + G_{33}H_z)^2}} \mu_B S_B. \quad (11)$$

$$M_3^z = \frac{g_{32}(G_{22}H_y + G_{23}H_z) + g_{33}(G_{32}H_y + G_{33}H_z)}{\sqrt{G_{11}^2H_x^2 + (G_{22}H_y + G_{23}H_z)^2 + (G_{32}H_y + G_{33}H_z)^2}} \mu_B S_B. \quad (12)$$

La structure magnétique correspondant au cas général est donc caractérisée par une configuration pyramidale des ions des sites B .

La base de cette pyramide est de forme trapézoïdale irrégulière et les longueurs des moments des ions B ne sont pas identiques. On vérifie aisément que la résultante R_B des moments B n'est pas colinéaire à S_A .

La forme de la pyramide, les longueurs des moments B et l'angle de R_B avec S_A sont des fonctions de la direction de H_A dans l'espace cristallin.

On voit donc que dans le cas général il peut exister dans les spinelles quadratiques des structures magnétiques non colinéaires très complexes lorsque l'on tient compte des anisotropies locale et d'échange.

(3.1.2) *Spinelles cubiques.* Un calcul analogue à celui effectué dans le cas du spinelle quadratique mais en considérant cette fois les tenseurs d'anisotropie relatifs aux spinelles cubiques conduit aux conditions d'équilibre:

$$\begin{aligned} \frac{\partial E}{\partial H_x} = 0 &= \frac{1}{3}(G_{11}^2 - G_{22}^2) \left[\left(\frac{1}{\alpha} + \frac{1}{\beta} \right) H_x \right. \\ &\quad - \left(\frac{1}{\gamma} + \frac{1}{\delta} \right) H_x + \sqrt{2} \left(\frac{1}{\alpha} - \frac{1}{\beta} \right) \frac{H_x H_y}{H_z} \\ &\quad \left. - \sqrt{2} \left(\frac{1}{\delta} - \frac{1}{\gamma} \right) \left(H_z - \frac{H_x^2}{H_z} \right) \right]. \quad (13) \end{aligned}$$

Ces équations sont une forme simplifiée de l'équation (6) et il existe donc a priori une solution générale où H_x , H_y et H_z sont tous différents de zéro. On obtient les composantes des moments de la même façon que pour les spinelles quadratiques et la structure magné-

tique aussi définie est tout à fait semblable à celle déjà décrite dans le quadratique.

(3.1.3) *Remarques.* Les configurations magnétiques possibles dans le cas général sont très complexes et il est difficile de suivre leur comportement en présence d'un champ magnétique extérieur. Il est donc plus avantageux de décrire quelques cas particuliers plus simples se rapprochant de résultats expérimentaux.

Il faut remarquer également que les équations $\partial E / \partial H_x = \partial E / \partial H_y = 0$ conduisent à des relations de la forme:

$$f(H_x, H_y, H_z) = 0, \quad f(H_x, H_y, -H_z) = 0$$

$$f(H_y, H_x, H_z) = 0, \quad f(H_y, H_x, -H_z) = 0$$

et ceci pour un quart de l'espace du cristal.

A un système H_x , H_y , H_z minimisant l'énergie, correspondent donc dans le cas général: 16 directions équivalentes de H_A à chacune desquelles est associée une structure magnétique semblable et d'énergie égale mais les dispositions relatives des moments des ions B ne sont pas les mêmes quand on passe d'une direction de H_A à une autre. Ceci est très facile à vérifier en calculant les composantes des moments des sites B pour les différentes directions possibles de H_A .

Les domaines magnétiques existant à champ extérieur nul dans un monocristal ne sont pas uniquement caractérisés par une direction de facile aimantation mais aussi par une configuration propre des moments des ions B .

(3.2) Solutions particulières: $H_y = 0$

Nous allons décrire ici quelques solutions particulières proches de résultats expérimentaux.

(3.2.1) *Spinelles quadratiques.* Supposons que les valeurs des paramètres G_{ij} soient telles qu'une structure magnétique ait son énergie minimale pour $H_y = 0$. Les équations (4) et (5) n'entraînent aucune solution particulière pour H_x et H_z .

La direction de H_A donc de S_A est contenue dans le plan (010). Cherchons pour une direction donnée de H_A quelle configuration adoptent les moments B . Il suffit de calculer les composantes de chacun des moments B : (cf. équations 10-11 et 12). On obtient les relations:

$$\begin{cases} M_3^x = M_4^x \\ M_3^y = -M_4^y \text{ et } M_5^y = M_6^y = 0 \\ M_3^z = M_4^z \end{cases}$$

M_3^x , M_5^z , M_6^x et M_6^z ont des valeurs toutes distinctes et différent aussi de celles des composantes de M_3 et M_4 .

La structure magnétique correspondante est donc caractérisée par la configuration des moments B suivante:—Les moments M_3 et M_4 sont de longueur égale et sont disposés symétriquement par rapport au plan (010).—Les moments M_5 et M_6 ne sont pas de longueur égale entre eux et n'ont pas non plus celle de M_3 et M_4 ; ils sont contenus dans le plan (010).—Les résultantes: $M_3 + M_4$ et $M_5 + M_6$ contenues dans le plan (010) ne sont pas colinéaires entre elles et aucune ne l'est non plus avec S_A . Le résultante générale $R_B = M_3 + M_4 + M_5 + M_6$ n'est pas non plus colinéaire à S_A .

La configuration magnétique correspondant à $H_y = 0$, représentée Fig. 1, est donc de type pyramidal distordu et elle n'admet comme élément de symétrie qu'un plan (010). Cette structure extrêmement complexe a été trouvée expérimentalement dans le cas de FeMn_2O_4 [8] bien que la diffraction des neutrons sur poudre n'ait pas permis de raffiner les paramètres.

(3.2.2) *Spinelles cubiques.* Si $H_y = 0$ corres-

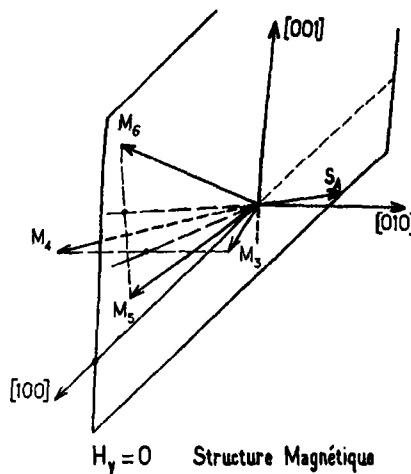


Fig. 1. Configuration magnétique en forme de pyramide distordue correspondant à la solution $H_y = 0$, H_x et H_z différents de zéro.

pond à un minimum de l'énergie, l'équation (11) qui représente la condition de stabilité devient:

$$\frac{\partial E}{\partial H_x} = \frac{1}{3} (G_{11}^2 - G_{22}^2) \left[\frac{2H_x}{\alpha} - H_x \left(\frac{1}{\gamma} + \frac{1}{\delta} \right) + \sqrt{2} \left(H_z - \frac{H_x^2}{H_z} \right) \left(\frac{1}{\gamma} - \frac{1}{\delta} \right) \right] = 0. \quad (14)$$

Il n'y a pas de relation simple entre H_x et H_z et il peut donc exister une solution dans le plan $H_y = 0$, c'est-à-dire en revenant au système d'axes naturels du cube, dans les plans de la forme (110).

En calculant de la même manière que précédemment les composantes des moments des ions B pour une direction donnée de H_A dans le plan $H_y = 0$, on trouve exactement les mêmes relations que dans le cas des spinelles quadratiques (cf. 3.2.1).

La configuration des moments magnétiques est donc tout à fait semblable à celle trouvée dans le cas précédent et la Fig. 1 qui la représente dans le cas général quadratique est également valable pour le cubique à condition de remplacer les axes cristallographiques [100] et [010] du système quadra-

tique par $[110]$ et $[110]$ respectivement, pour le système cubique.

(3.2.3) *Remarques.* Il est intéressant de voir que dans le cas où $H_y = 0$ est une solution stable, les spinelles cubiques et quadratiques se comportent de la même manière. Il existe des solutions encore plus particulières dans ce plan: celles qui correspondent à des directions cristallographiques simples: $[100]$ et $[001]$ dans le quadratique et $[110]$, $[111]$ et $[001]$ dans les spinelles cubiques.

(3.2.4) *La direction $[100]$ du quadratique* (ou $[110]$ du cubique) est caractérisée par la relation supplémentaire: $H_z = 0$. En annulant donc H_z dans l'expression des composantes des moments B , on est conduit aux relations suivantes:

$$\begin{cases} M_3^x = M_4^x \\ M_3^y = M_3^z = M_4^y = M_4^z = 0 \end{cases}$$

et

$$\begin{cases} M_5^x = M_6^x \\ M_5^y = M_6^y = 0. \\ M_5^z = -M_6^z \end{cases}$$

La structure magnétique correspondante est beaucoup plus simple que dans le cas général, en effet:—les moments M_3 et M_4 (de longueur égale) sont colinéaires à S_A suivant l'axe Ox (direction $[100]$ du quadratique ou $[110]$ de cubique)—les moments M_5 et M_6 sont dans le plan xOz et symétriques par rapport à l'axe Ox . Cette configuration magnétique est représentée Fig. 2.

(3.2.5) *La direction $[001]$ (cubique et quadratique)* est caractérisée par la relation supplémentaire $H_x = 0$ qui entraîne pour les composantes des moments B les relations suivantes:

$$\begin{cases} M_3^x = M_4^x = M_5^y = M_6^y = 0 \\ M_3^y = -M_4^y = -M_5^x = M_6^x \\ M_3^z = M_4^z = M_5^z = M_6^z. \end{cases}$$

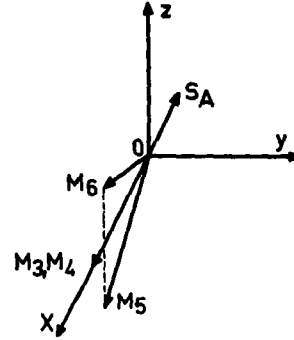


Fig. 2. Configuration magnétique correspondant à la solution particulière $H_y = H_z = 0$ et $H_x = H_A$.

La structure particulière correspondante est donc caractérisée par un arrangement pyramidal régulier des moments B (de longueur identique) d'axe de symétrie $[001]$. La résultante des moments B est colinéaire à S_A . Cette configuration magnétique est représentée Fig. 3.

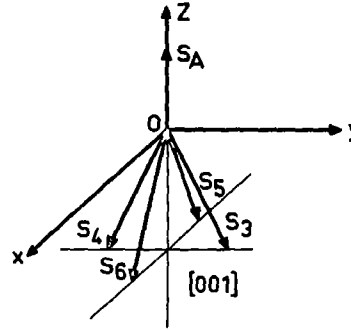


Fig. 3. Configuration magnétique correspondant à $H_x = H_y = 0, H_z = H_A$.

(3.2.6) *La direction $[111]$ dans le système cubique* est une direction très particulière qui n'a pas d'équivalent dans le système quadratique. Elle est caractérisée par la relation $H_x = \sqrt{2}H_z = (\sqrt{2}/\sqrt{3})H_A$.

Il est intéressant dans ce cas d'explicitier les composantes des moments M_B :

$$\begin{cases}
 M_3^x = M_4^x = \frac{3\sqrt{2}g_{11}G_{11}}{\sqrt{3}\sqrt{8G_{11}^2 + G_{22}^2}} \mu_B S_B \\
 M_3^y = -M_4^y = \frac{g_{22}G_{22} - g_{11}G_{11}}{\sqrt{3}\sqrt{8G_{11}^2 + G_{22}^2}} \mu_B S_B \\
 M_3^z = M_4^z = \frac{1}{\sqrt{3}} \frac{2g_{11}G_{11} + g_{22}G_{22}}{\sqrt{8G_{11}^2 + G_{22}^2}} \mu_B S_B \\
 \\
 M_5^x = \frac{\sqrt{2}2g_{11}G_{11} + g_{22}G_{22}}{\sqrt{3}\sqrt{8G_{11}^2 + G_{22}^2}} \mu_B S_B \\
 M_5^y = 0 \\
 M_5^z = \frac{1}{\sqrt{3}} \frac{4g_{11}G_{11} - g_{22}G_{22}}{\sqrt{8G_{11}^2 + G_{22}^2}} \mu_B S_B \\
 \\
 M_6^x = \frac{\sqrt{2}}{\sqrt{3}} g_{22} \mu_B S_B \\
 M_6^y = 0 \\
 M_6^z = \frac{1}{\sqrt{3}} g_{22} \mu_B S_B.
 \end{cases}$$

On constate immédiatement que M_6 est colinéaire à S_A et si l'on calcule la résultante générale des moments B : $R_B = M_3 + M_4 + M_5 + M_6$ on la trouve également colinéaire à S_A .

Cette structure magnétique est donc extrêmement curieuse car bien que les moments B soient de longueur inégale et occupent des positions non particulières ni dans l'espace cristallin ni par rapport à S_A (sauf M_6), leur résultante R_B est alignée avec S_A . Cette configuration est représentée Fig. 4.

(3.3) Solutions particulières $H_x = 0$

Il est intéressant de voir quelles solutions peuvent exister lorsque l'énergie du système est minimum pour $H_x = 0$ c'est-à-dire S_A dans un plan de base.

(3.3.1) *Spinelles quadratiques*. La condition d'équilibre $\partial E / \partial H_x = 0$ s'écrit dans ces conditions:

$$(G_{11}^2 - G_{22}^2 - G_{32}^2) H_x \left(\frac{1}{\alpha} - \frac{1}{\gamma} \right) = 0$$

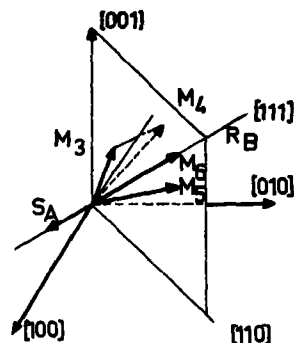


Fig. 4. Configuration magnétique correspondant à la solution très particulière où H_A est parallèle à la direction $[111]$ dans un spinelle cubique.

en supposant $(G_{11}^2 - G_{22}^2 - G_{32}^2) \neq 0$ deux solutions sont évidentes:

(1) $H_x = 0$ qui, joint à $H_z = 0$, conduit à une solution tout à fait semblable à celle décrite pour $H_y = H_z = 0$ (voir 3.2.4)

(2) $1/\alpha - 1/\beta = 0$ ceci entraîne $H_x = H_y = H_A/\sqrt{2}$.

Les moments S_A sont donc dirigés suivant une direction $[110]$ du spinelle quadratique.

Les composantes des moments B correspondant à cette solution obéissent aux relations:

$$\begin{cases}
 M_3^x = M_4^x = M_5^y = M_6^y \\
 M_3^y = M_4^y = M_5^x = M_6^x \\
 M_3^z = -M_4^z = -M_5^z = M_6^z.
 \end{cases}$$

La structure magnétique a donc les caractéristiques suivantes:

(a) les moments des sites A sont parallèles à la direction $[110]$

(b) les moments des sites B -de longueur identique- sont divisés en 4 sous-réseaux formant une pyramide d'axe $[110]$ et comportant comme plans de symétrie les plans (001) et (110) . Cette configuration est représentée Fig. 5.

(3.3.2) *Spinelles cubiques*. L'équation d'équilibre $\partial E / \partial H_x = 0$ se réduit ici à:

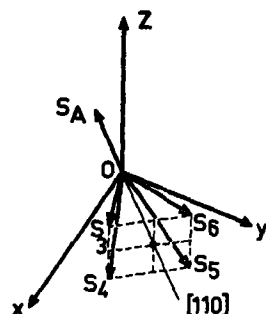


Fig. 5. Configuration magnétique correspondant à la solution $H_z = 0$ et $H_x = H_y = H_A/\sqrt{2}$.

$$(G_{22}^2 - G_{11}^2) H_x \left(\frac{1}{\alpha} - \frac{1}{\gamma} \right) = 0.$$

Les deux solutions trouvées dans le cas du système quadratique se retrouvent ici, les configurations magnétiques correspondantes sont les mêmes et il suffit de changer les directions $[100]$ et $[110]$ du quadratique en $[110]$ et $[100]$ respectivement pour être dans le système d'axes cristallographiques naturels du spinelle cubique.

(3.4) Solutions particulières $H_x = H_y$

(3.4.1) *Spinelles quadratiques*. La condition d'équilibre $\partial E / \partial H_x = 0$ s'écrit dans ce cas:

$$(G_{11}^2 + G_{22}^2 + G_{33}^2 - 2G_{23}^2 - 2G_{33}^2) \left(\frac{1}{\alpha} + \frac{1}{\beta} \right) H_x + (G_{22}G_{23} + G_{32}G_{33}) \left(\frac{1}{\alpha} - \frac{1}{\beta} \right) \left(H_z - \frac{2H_x^2}{H_z} \right) = 0 \quad (15)$$

qui même en appliquant la relation $H_A^2 = 2H_x^2 + H_z^2$ ne conduit pas à des solutions particulières en H_x ou H_z . Il existe donc une solution générale correspondant à une direction quelconque de S_A dans le plan (110) .

La configuration des moments des ions des sites B correspondant à une direction donnée de S_A est caractérisée par les relations suivantes:

$$\begin{cases} M_3^x = M_6^y \\ M_3^y = M_6^x \\ M_3^z = M_6^z \end{cases} \text{ et } \begin{cases} M_4^x = M_5^y \\ M_4^y = M_5^x \\ M_4^z = M_5^z \end{cases}$$

Les moments B forment donc une pyramide de base trapézoïdale admettant le plan $(1\bar{1}0)$ comme plan de symétrie. La forme de la pyramide est d'ailleurs fonction de sa direction dans l'espace (Fig. 6).

Les solutions limites correspondent d'une part à $S_A \parallel [001]$ et celle-ci a déjà été décrite en (3.2.5) et d'autre part à $S_A \parallel [110]$ également déjà décrite en (3.3.1).

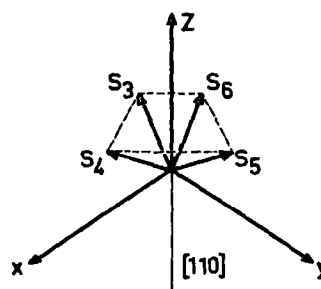


Fig. 6. Configuration magnétique correspondant à $H_x = H_y$ et $H_z \neq 0$.

(3.4.2) *Spinelles cubiques*. La condition d'équilibre se réduit à:

$$(G_{22}^2 - G_{11}^2) \left(H_z - \frac{2H_x^2}{H_z} \right) \left(\frac{1}{\alpha} - \frac{1}{\beta} \right) = 0$$

ce qui conduit à deux solutions seulement:

(1) $1/\alpha - 1/\beta = 0$ qui entraîne $H_z = 0$. Ce cas a déjà été décrit en (3.3.1) et (3.3.2).

(2) $H_z - 2H_x^2/H_z = 0$ soit $H_z = \sqrt{2} H_x$. Dans ce cas S_A est dirigé suivant une direction $[101]$ de cube. Cette solution est évidente car elle est tout à fait semblable à celle trouvée pour une direction cristallographique équivalente: $[110]$ en (3.3.1) et (3.3.2).

4. REMARQUES

L'étude des structures magnétiques possibles engendrées par l'anisotropie dans les

spinelles quadratiques et cubiques et dans le cadre des hypothèses formulées au début du chapitre II, montre qu'il existe des configurations de spins non colinéaires et même parfois très complexes. L'intérêt de ce développement est qu'il démontre qu'il n'est pas besoin de considérer des interactions BB du même ordre de grandeur que les interactions AB pour qu'existe une structure non-linéaire et en particulier une structure de type Yafet-Kittel (cas particulier d'une structure pyramidale).

Il est très important de remarquer qu'à une structure magnétique anisotrope donnée dans une direction donnée et déterminée par son énergie, correspondent d'autres structures d'énergie égale dans des directions cristallographiques équivalentes. *Mais les dispositions relatives des moments des quatre sous-réseaux B sont différentes* (cf. 3.1.3). Il n'est pas possible de retrouver ce résultat par un calcul de champ moléculaire sans tenir compte de l'anisotropie. Or des études expérimentales par diffraction de neutrons [6-8] ont montré indiscutablement que les configurations des moments B dépendaient de leur direction dans le cristal.

La détermination de structures par le calcul exposé ici entraîne automatiquement l'existence d'anisotropie. Ceci peut sembler évident mais montre bien la différence d'origine de structures non-linéaires et partant de leurs propriétés. Celles ayant pour origine l'anisotropie, en comportent obligatoirement alors que celles ayant pour origine de fortes interactions BB ne peuvent avoir qu'une anisotropie faible, sinon on retombe automatiquement dans le traitement précédent.

Le comportement de ces deux types de structure est très différent lorsqu'un champ extérieur est appliqué comme nous allons le voir au chapitre suivant et ceci est un critère de distinction.

5. COMPORTEMENT D'UNE CONFIGURATION MAGNETIQUE ANISOTROPE EN PRESENCE D'UN CHAMP EXTERIEUR

Les configurations magnétiques anisotropes que nous venons de définir sont étroitement liées à leurs directions dans l'espace cristallin, il est donc très intéressant de suivre leurs comportements lorsqu'un champ magnétique extérieur est appliqué et les force à changer leur orientation.

(5.1) Cas général

Nous avons déjà écrit l'énergie minimale par rapport aux spins S_B en présence d'un champ extérieur: équation (3). Il est possible de déterminer la direction stable de S_A en présence de champ extérieur, en minimisant cette énergie par rapport à S_A (ou H_A) et en procédant de la même façon c'est-à-dire en dérivant par rapport aux composantes sur les axes, on aboutit en tenant compte de la $\sum_i (S_A^i)^2 = S_A^2$ à deux équations: $\partial E / \partial S_A^x = 0$ et $\partial E / \partial S_A^z = 0$ par exemple, qui donnent directement la relation entre S_A (ou H_A) et H_0 , par l'intermédiaire de leurs composantes.

Dans le cas général ces relations sont extrêmement compliquées mais permettent théoriquement de résoudre complètement le système en fonction de la valeur de H_0 . Il devient en effet possible de calculer ensuite toutes les composantes des divers moments M_B qui s'écrivent:

$$M_{Bk}^i = \mu_B \sum g_{ij} S_{Bk}^i$$

$$= \mu_B \frac{\sum_j g_{ij} \sum_i (H_A^i G_{ij} + H_0^i g_{ij})}{\sqrt{\sum_j \left[\sum_i (H_A^i G_{ij} + H_0^i g_{ij}) \right]^2}} S_B \quad (16)$$

Pour donner une idée de la complexité des expressions écrivons par exemple la composante du moment M_3 sur Oz dans le cas d'un spinelle quadratique:

$$M_3^z = \frac{g_{23}(G_{22}H_y + G_{23}H_z + g_{22}H_0^y + g_{23}H_0^z) + g_{33}(G_{32}H_y + G_{33}H_z + g_{32}H_0^y + g_{33}H_0^z)}{\sqrt{(G_{11}H_x + g_{11}H_0^x)^2 + (G_{22}H_y + G_{23}H_z + g_{22}H_0^y + g_{23}H_0^z)^2 + (G_{32}H_y + G_{33}H_z + g_{32}H_0^y + g_{33}H_0^z)^2}} \mu_B S_B$$

Toutes les autres composantes sont aussi compliquées et il n'est pas intéressant de vouloir discuter dans le cas général. Il est par compte beaucoup plus facile de voir ce qu'il se passe lorsque le champ magnétique est appliqué suivant des directions cristallographiques simples et dans des cas de configurations magnétiques correspondant à des solutions particulières à champ nul.

Les cas que nous allons étudier sont pris dans le système quadratique et proches de résultats expérimentaux qui seront publiés prochainement:

(a) cas de la structure pyramidale distordue de plan de symétrie (010), H_0 étant appliqué suivant la direction [010]

(b) cas de la structure pyramidale d'axe [110], le champ H_0 étant appliqué successivement suivant les directions [001] et [100].

(5.2) Structure pyramidale distordue de plan de symétrie (010)

Cette structure définie au section (3.2.1) et représentée Fig. 1 est caractérisée par la seule condition particulière à champ nul:

$$H_y = 0.$$

(5.2.1) H_0 parallèle à la direction [010]. Les composantes H_0^x et H_0^z du champ H_0 sont nulles. En appliquant les conditions d'équilibre $\partial E / \partial H_A^j = 0$, on ne trouve pas de relations simples entre les composantes de H_A et celles de H_0 mais il est tout de même possible de décrire le type d'évolution de la structure magnétique en étudiant les variations avec H_A et H_0 des diverses composantes des moments magnétiques B . Sans entrer dans les calculs compliqués, la Fig. 7 donne quelques phases de l'évolution de la configuration des moments B lorsque H_0 croît. On peut voir que la pyramide qui existait à champ nul se transforme complètement au fur et à mesure du changement de son orientation pour aboutir finalement quand H_0 devient grand par rapport à l'anisotropie à une configuration limite analogue à celle déjà trouvée en (3.2.4) (Fig. 2).

(5.3.) Structure pyramidale d'axe [110]

Cette structure a été définie au paragraphe (3.3.1) et est caractérisée à champ nul par $H_x = 0$ et $H_x = H_y = H_A / \sqrt{2}$.

(5.3.1) H_0 parallèle à la direction [001]. On a évidemment dans ce cas $H_0^x = H_0^y = 0$

En remplaçant dans l'équation 3 les composantes sur Oy de H_A (et S_A), en fonction de celles sur Ox et Oz et en appliquant les conditions d'équilibre, on voit immédiatement que $H_x = H_y$ rend identiquement nulle l'équation $\partial E / \partial H_x$ et qu'alors l'équation $\partial E / \partial H_A = 0$ donne une relation entre H_A et H_0 . L'on voit donc bien que partant d'une structure dirigée à champ nul suivant la direction [110], l'application d'un champ magnétique suivant la direction [001] fait déplacer S_A dans le plan (110) (c'est-à-dire $H_x = H_y$ quel que soit H_0) puisque cette solution correspond au minimum de l'énergie.

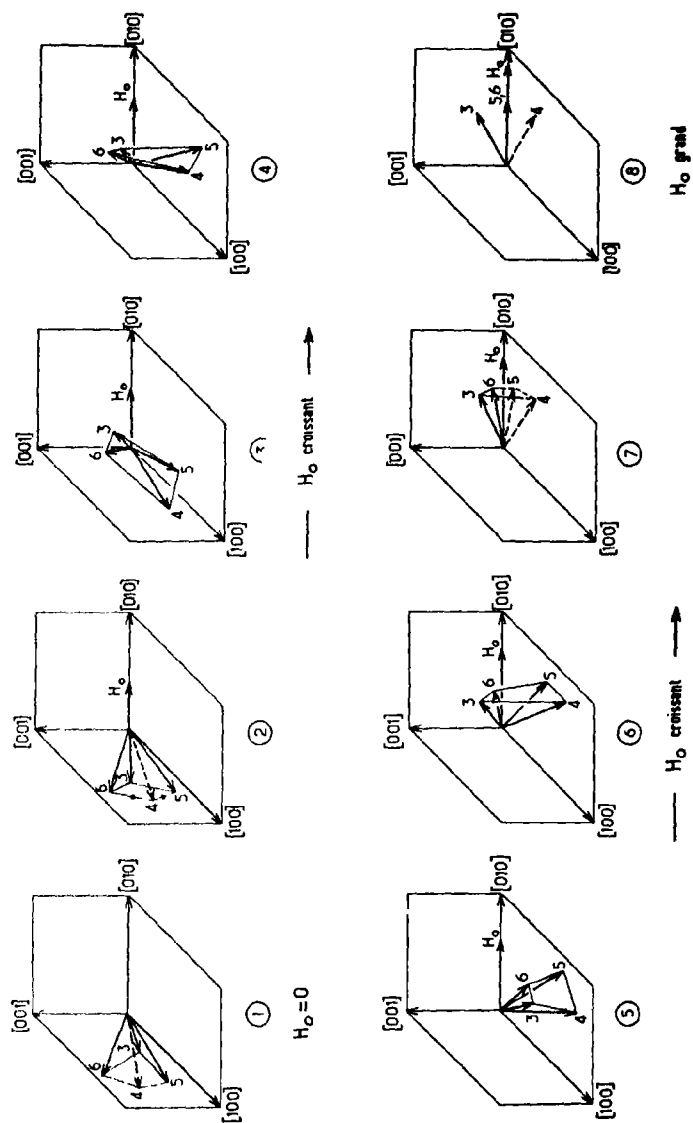
Sans écrire ici les expressions détaillées des composantes des moments B on a toujours entre elles les relations suivantes:

$$\begin{cases} M_3^x = M_6^y \\ M_3^y = M_6^x \\ M_3^z = M_6^z \end{cases} \text{ et } \begin{cases} M_4^x = M_5^y \\ M_4^y = M_5^x \\ M_4^z = M_5^z \end{cases}$$

La configuration magnétique reste donc toujours symétrique par rapport au plan (110). La Fig. 8 présente quelques états intermédiaires de la configuration des moments B en fonction de l'intensité croissante de H_0 . Lorsque H_0 est devenu suffisamment grand par rapport à l'anisotropie les relations entre composantes des moments deviennent à la limite:

$$\begin{cases} M_3^x = M_6^y = M_4^x = M_5^y = 0 \\ M_3^y = M_6^x = -M_4^y = -M_5^x \\ M_3^z = M_6^z = M_4^z = M_5^z \end{cases}$$

c'est une pyramide de base carrée et ayant pour axe de symétrie la direction [001]. La



Evolution des Moments B_i en fonction de champ extérieur H_0

Fig. 7. Evolution de la configuration des moments B_i — d'une solution $H_s = 0$ à champ nul — en fonction de l'intensité croissante du champ extérieur H_0 appliqué suivant la direction $[010]$ d'un spinelle quadratique.

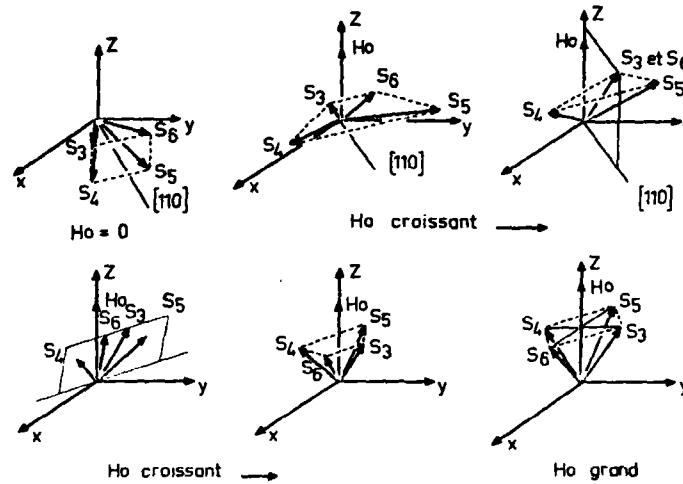


Fig. 8. Evolution de la configuration des moments B — d'une solution $H_x = 0$ et $H_x = H_y$ à champ nul — en fonction de l'intensité croissante du champ extérieur H_0 appliqué suivant la direction $[001]$ d'un spinelle quadratique.

disposition des moments est tout à fait analogue à celle de la structure décrite en (3.2.5) (Fig. 3).

L'évolution de la structure entre les deux limites correspondant à $H_0 = 0$ et H_0 grand est intéressante à suivre. En effet, on peut tout d'abord remarquer que M_4^z et M_5^z s'annulent pour une certaine valeur de champ, ceci est naturel car les moments M_4 et M_5 étaient au-dessous du plan de base à champ nul.

Pour une autre valeur du champ appliqué, M_4^y et M_5^x s'annulent, les moments M_4 et M_5 sont contenus alors les plans (010) et (100) respectivement; les moments M_3 et M_6 sont toujours symétriques par rapport au plan $(\bar{1}10)$ mais n'occupent pas de positions particulières. H_0 continuant à croître les quatre moments deviennent coplanaires après que deux d'entre eux (M_3 et M_6) soient devenus parallèles et dans le plan $(\bar{1}\bar{1}0)$.

(5.3.2) H_0 parallèle à la direction $[100]$. Les composantes H_0^y et H_0^z sont donc nulles. On vérifie aisément comme dans le cas précédent que partant à champ nul d'une structure où $H_x = 0$, en appliquant la champ

H_0 suivant la direction $[100]$ la composante H_x restant nulle correspond bien au minimum de l'énergie puisque $\partial E / \partial H_x$ est identiquement nul quel que soit H_0 et $\partial E / \partial H_x = 0$ donne la relation entre H_A et H_0 . Lorsque l'on fait croître le champ extérieur depuis une valeur nulle, les moments des sites A restent donc dans le plan (001) .

Sans expliciter ici les valeurs des composantes des moments B en fonction du champ extérieur, les relations suivantes sont toujours vérifiées:

$$\begin{cases} M_3^x = M_4^x \\ M_3^y = M_4^y \text{ et } \\ M_3^z = -M_4^z \end{cases} \quad \begin{cases} M_5^x = M_6^x \\ M_5^y = M_6^y \\ M_5^z = -M_6^z. \end{cases}$$

La configuration magnétique admet donc toujours le plan (001) comme plan de symétrie quelle que soit la valeur de H_0 .

En supposant H_0 suffisamment grand par rapport à l'anisotropie, les composantes des moments B deviennent à la limite:

$$\left\{ \begin{array}{l} M_3^x = M_4^x = g_{11} \mu_B S_B \\ M_3^y = M_4^y = 0 \\ M_3^z = M_4^z = 0 \end{array} \right. \quad \text{et} \quad \left\{ \begin{array}{l} M_5^x = M_6^x \\ M_5^y = M_6^y = 0 \\ M_5^z = -M_6^z \end{array} \right.$$

M_5^x et M_5^z sont des fonctions de H_0 . Les moments M_3 et M_4 tendent à devenir tous deux parallèles à la direction $[100]$ alors que les moments M_5 et M_6 viennent se placer symétriquement par rapport à la direction $[100]$ dans le plan (010) . L'angle entre M_5 et la direction $[100]$ est fonction de l'intensité de H_0 .

La Fig. 9 schématise le comportement de cette configuration tel qu'il vient d'être décrit.

structures de même énergie dirigées suivant des directions équivalentes de l'espace cristallin. Ces structures sont globalement identiques, la seule différence étant que pour chaque direction existe un arrangement différent des moments B . Il est évident et très facile de vérifier par le calcul, que les déformations des structures équivalentes sous l'action d'un champ extérieur dirigé de la même manière relative par rapport à chacune d'elles, sont les mêmes. Il suffit dans chaque cas de considérer la configuration de moments B correspondante.

Si maintenant au lieu d'examiner l'action d'un champ dirigé de la même manière relative par rapport à des structures équivalentes,

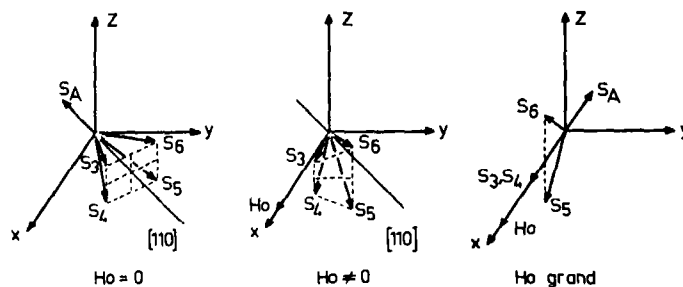


Fig. 9. Evolution de la configuration des moments B — d'une solution $H_x = 0$ et $H_z = H_0$ à champ nul — en fonction de l'intensité croissante du champ extérieur H_0 appliqué suivant la direction $[100]$ d'un spinelle quadratique.

(5.4) Remarques

L'évolution des configurations magnétiques en présence d'un champ extérieur n'a été décrite ici que dans quelques cas particuliers et il faut bien noter que les figures qui les représentent, ne sont que des modèles. En effet, les valeurs relatives des paramètres g_{ij} et G_{ij} conditionnent les déformations de la structure et peuvent évidemment modifier l'ordre de la succession des phases intermédiaires comme par exemple celles de la Fig. 8.

D'autre part, nous avons toujours examiné des structures contenues dans un seul octant de l'espace cristallin. Or comme nous l'avons déjà fait remarquer, il existe naturellement des

envisageons l'action d'un champ sur un monocristal. Pour plus de simplicité prenons un spinelle quadratique ayant la structure magnétique définie au (3.3.1) c'est-à-dire une pyramide d'axe $[110]$. Dans un monocristal d'un tel spinelle, existent donc quatre domaines magnétiques correspondant aux quatre directions équivalentes à la $[110]$, chacun de ces domaines est caractérisé par une configuration de moments B (Fig. 10). Appliquons le champ extérieur H_0 suivant la direction $[100]$. La structure dirigée suivant la $[110]$ va se comporter comme cela a été décrit Fig. 9. La structure dirigée suivant la direction $[1\bar{1}0]$ (qui n'a pas le même groupement de moments: M_3 et M_4 sont permutés) subit les mêmes

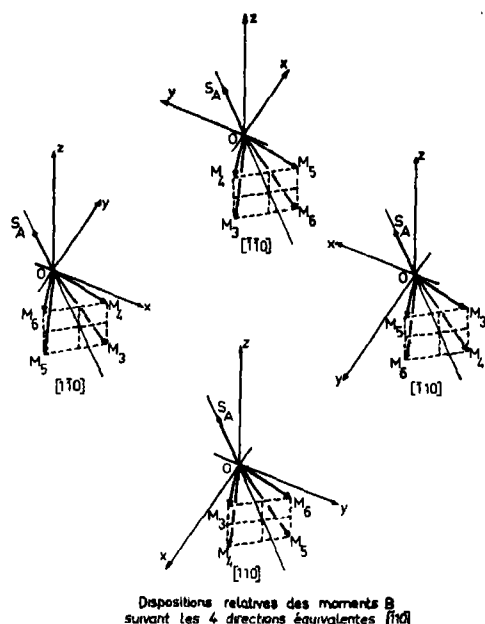


Fig. 10. Disposition des moments M_k dans les quatre configurations d'énergie égale mais dont les axes de symétrie à champ extérieur nul sont les quatre directions cristallographiques équivalentes de la forme $[110]$ dans un spinelle quadratique.

déformations globales mais par rapport à la précédente: M_3 et M_4 sont constamment symétriques de leurs homologues par rapport à l'axe $[100]$, M_5 et M_6 eux, sont toujours symétriques de leurs homologues par rapport au plan (010) . Lorsque H_0 est devenu suffisamment grand, les deux structures sont confondues dans le plan (010) (cf. Fig. 9).

De la même manière, il est aisé de voir et de calculer que les deux autres structures dirigées suivant les directions $[\bar{1}\bar{1}0]$ et $[\bar{1}10]$ se rapprochent progressivement des plans (100) et (010) respectivement, passent par les directions $[1\bar{1}0]$ et $[\bar{1}10]$ respectivement où elles retrouvent des groupements de moments analogues à ceux des structures qui y existaient à champ nul et enfin viennent se confondre avec les deux autres dans le plan (010) pour ne plus former qu'un monodomaine de structure magnétique unique.

Il y a donc une solution de continuité dans l'espace entre les structures équivalentes qui se transforment l'une en l'autre si le champ magnétique extérieur les oblige à changer de direction.

6. CONCLUSION

Dans le cadre d'hypothèses simples, il a été développé un calcul de champ moléculaire qui fait intervenir l'anisotropie comme élément principal dans les spinelles cubiques et quadratiques. Parmi toutes les solutions générales ou particulières décrites ici, une seule peut naturellement exister dans un cas donné: c'est celle ayant l'énergie minimale. Il eut été possible de faire une discussion suivant les valeurs relatives des G_u et g_u sur les domaines de stabilité des différentes structures, mais les expressions sont si compliquées qu'il eût été sans intérêt de formuler des inégalités trop complexes.

L'intérêt de ce développement est qu'il permet à partir de structures—solutions des équations d'équilibre—d'analyser leur comportement en présence d'un champ extérieur, ce que ne permet pas la théorie des groupes. L'étude de l'évolution des configurations magnétiques quand un champ est appliqué montre bien la différence entre des structures définies sans tenir compte de l'anisotropie et celles où l'anisotropie est un facteur de base. Une structure telle que celle définie par Yafet et Kittel par exemple ne peut avoir ces propriétés et nous verrons que dans le cas des manganites spinelles[10], l'expérience confirme l'existence d'un tel comportement.

Remerciements—Nous remercions Monsieur le Professeur Herpin qui a suivi de près ce travail et Monsieur Meriel qui nous a aidés par de nombreuses discussions.

REFERENCES

1. NEEL L., *Ann. Phys.* 3, 137 (1948).
2. YAFET Y. and KITTEL C., *Phys. Rev.* 87, 290 (1952).
3. BOUCHER B., BUHL R. and PERRIN M., *J. Phys. Chem. Solids* 31, 3 (1970).
4. VILLAIN J., *J. Phys. Chem. Solids* 11, 303 (1959).
5. MORIYA T., *Phys. Rev.* 117, 635 (1960).
6. BOUCHER B., BUHL R. and PERRIN M., *J. appl. Phys.* 39, 632 (1968).

7. BOUCHER B., BUHL R. and PERRIN M., *J. Phys. Chem. Solids* **31**, 363 (1970).
8. BOUCHER B., BUHL R. and PERRIN M., *J. appl. Phys.* **40**, 1126 (1969).
9. DWIGHT K. and MENYUK N., *Phys. Rev.* **119**, 1470 (1960).
10. BOUCHER B., BUHL R. and PERRIN M., to be published.

A GREEN FUNCTION APPROACH TO THE PROBLEM OF TWO MAGNETIC IMPURITIES IN A NON-MAGNETIC METAL

T. GAVAN and B. G. S. DOMAN

Department of Applied Mathematics, The University of Liverpool, Liverpool, England

(Received 2 June 1969; in revised form 23 September 1969)

Abstract—The method of double-time Green Functions is used to investigate a system of two magnetic impurities. It is found that the quasibound state at the Fermi surface of the isolated impurities splits into two, symmetrically spaced either side of the Fermi surface, when the separation becomes finite. T_c is shown to be independent of the impurity separation and the two impurity contributions to the resistivity is calculated for $T \sim 0$ within the approximation that the separation is not small. The resistivity of the interacting system is found to be less than for two isolated impurities. This result is extended to a real alloy by summing over impurity sites in pairs.

INTRODUCTION

SINCE Kondo's paper[1] was published in 1964, great interest has been shown in the problems posed by dilute magnetic alloys. The $s-d$ exchange model has been the most prominent starting point for authors in this field. In particular, Nagaoka[2] used the method of double-time Green Functions to obtain Kondo's result and show that the singular $\log T$ behaviour disappears at low temperatures. Takano and Ogawa[3] simplified the solution of the equations of motion for the Green Function by second quantising the impurity spin operator and using an alternative decoupling scheme. In the main, concentrations have been assumed to be small enough for interactions between impurities to be neglected, so that each impurity could be treated individually. Notable exceptions have been Breseman and Bailyn[4], who used Nagaoka's procedure on the two impurity system to extract the $RKKY$ interaction, and *M. J. Beal-Monod*[5] who has calculated the two impurity resistivity in the region of the Kondo minimum.

Nagaoka extended his original paper to take into account moderate concentrations[6] by using a multi-impurity Hamiltonian. He found,

among other things, that his T_c was independent of the concentration, and this result is reproduced here. However, he took an average over the impurity sites before solving the equations of motion, thereby removing the effect of correlations between impurities.

Here, we use a Takano and Ogawa's procedure[3] to investigate in detail a system of two impurities below the critical temperature T_c . It is found that, for a finite separation, two quasibound states exist below T_c , as opposed to one in the single impurity system, and that T_c is independent of impurity separation. The relaxation time and the 2-impurity contribution to the resistivity are calculated as a function of the distance between the impurities for large separations and temperatures close to zero. It is found that the correction due to the finite separation causes the resistivity to be reduced.

In the last section resistivity of a real alloy is estimated by summing over impurity sites in pairs.

1. HAMILTONIAN

Using the $s-d$ exchange model, the Hamiltonian for a system of two localised spins situated in $\mathbf{R}_1$ and $\mathbf{R}_2$ interacting with the

conduction electrons is

$$H = \sum_{l\sigma} \epsilon c_{l\sigma}^\dagger c_{l\sigma} - \frac{J}{2N} \sum_{n=1}^2 \sum_{ll'} e^{i(l'-l) \cdot R_n} ((c_{l+}^\dagger + c_{l-}^\dagger - c_{l+}^\dagger - c_{l-}^\dagger) S_z^n + c_{l+}^\dagger c_{l-} S_-^n + c_{l-}^\dagger c_{l+} S_+^n) \quad (1.1)$$

where N is the total number of atoms in the crystal and J is the strength of the exchange interaction and is negative for an antiferromagnetic coupling, which is the case we consider.

The impurity spin operators are second quantised as follows

$$S_z^n = \frac{1}{2}(a_{n+}^\dagger a_{n+} - a_{n-}^\dagger a_{n-}) \quad (1.2a)$$

$$S_+^n = a_{n+}^\dagger a_{n-} \quad (1.2b)$$

$$S_-^n = a_{n-}^\dagger a_{n+} \quad (1.2c)$$

where we have taken $S = \frac{1}{2}$ for simplicity.

The commutation rules are now given

$$\{C_{k\sigma}, C_{k'\sigma'}\}_+ = \delta_{kk'} \delta_{\sigma\sigma'}, \\ \{a_{n\sigma}, a_{n'\sigma'}\}_+ = \delta_{nn'} \delta_{\sigma\sigma'}, [a, c]_+ = 0. \quad (1.3)$$

2. GREEN FUNCTION AND EQUATIONS OF MOTION

We consider the Green Function [7]

$$G_{kk'}^{(\omega)} = \langle \langle c_{k+}, c_{k'}^\dagger \rangle \rangle \quad (2.1)$$

which satisfies the equation

$$(\omega - \epsilon_{k'} \pm i\delta) G_{kk'}^{(\omega)} (\omega \pm i\delta) = \frac{\delta_{kk'}}{2\pi} - \frac{J}{2N} \sum_{n=1}^2 \sum_l e^{i(l-k) \cdot R_n} \langle \langle c_{l+}, S_z^n + c_{l-} S_-^n | c_{k+}^\dagger \rangle \rangle \quad (2.2)$$

where the $\pm i\delta$ refer to the retarded and advanced forms. Henceforth, we suppress the $\pm i\delta$ except where significant.

Equation (2.2) introduces a higher order

Green Function on the right hand side. Obtaining the equation of motion for this $G.F.$ would bring in higher order $G.F.$'s still. So, we must simplify the equation by making a decoupling approximation. In this we follow Takano and Ogawa's [3] procedure, remembering that the average of an operator which does not conserve total spin vanishes, Nagaoka [2]. This was shown to be true for antiferromagnetic coupling by Takano and Ogawa [3].

The decoupling procedure gives:-

$$\langle \langle c_{l\sigma} a_{n\alpha}^\dagger a_{n\beta} | c_{k+}^\dagger \rangle \rangle = \langle a_{n\alpha}^\dagger a_{n\beta} \rangle \langle \langle c_{l\sigma} | c_{k+}^\dagger \rangle \rangle \delta_{\alpha\beta} + \langle c_{l\sigma} a_{n\alpha}^\dagger \rangle \langle \langle a_{n\beta} | c_{k+}^\dagger \rangle \rangle \delta_{\sigma\alpha}. \quad (2.3)$$

Therefore

$$(\omega - \epsilon_{k'}) G_{kk'}(\omega) \pm \frac{J}{2N} \sum_{n=1}^2 e^{-ik' \cdot R_n} [\langle S_z^n \rangle G_{nk} - (\frac{1}{2}\alpha_n^+ + \alpha_n^-) F_{nk}] = \frac{\delta_{kk'}}{2\pi} \quad (2.4)$$

where we have made the abbreviations

$$\alpha_n^+ = \sum_l e^{il \cdot R_n} \langle a_{n+}^\dagger c_{l+} \rangle \\ \alpha_n^- = \sum_l e^{il \cdot R_n} \langle a_{n-}^\dagger c_{l-} \rangle \\ G_{nk} = \sum_l e^{il \cdot R_n} G_{kl} \\ F_{nk} = \langle \langle a_{n+} | c_{k+}^\dagger \rangle \rangle. \quad (2.5)$$

If we remember that

$$\langle c_{l\sigma}^\dagger a_{n\sigma} \rangle = \langle a_{n\sigma}^\dagger c_{l\sigma} \rangle^* \quad (2.6)$$

then the equation of motion for F_{nk} and the equation for α_n , which will complete the set of self-consistent equations, are:

$$\omega F_{nk} + \frac{J}{2N} (\sigma_z^n F_{nk} - (\frac{1}{2}\bar{\alpha}_n^+ + \bar{\alpha}_n^-)) G_{nk} = 0 \quad (2.7)$$

and

$$\bar{\alpha}_n = i \int d(\omega) f(\omega) \sum_l (F_{nl}(\omega + i\delta) - F_{nl}(\omega - i\delta)) e^{-il \cdot R_n} \quad (2.8)$$

where

$$f(\omega) = \frac{1}{1 + e^{\omega/T}}.$$

The bar refers to the complex conjugate and the additional abbreviation

$$\sigma_z^n = \sum_{\sigma} e \quad \langle c_{I+}^{\dagger} c_{I+} - c_{I-}^{\dagger} c_{I-} \rangle \quad (2.9)$$

has been made.

In calculating (2.7) we have used the following decoupling procedure

$$\begin{aligned} \langle \langle c_{I\sigma}^{\dagger} c_{I\sigma} a_{n\alpha} | c_{k+}^{\dagger} \rangle \rangle &= \langle c_{I\sigma}^{\dagger} c_{I\sigma} \rangle \\ \langle \langle a_{n\alpha} | c_{k+}^{\dagger} \rangle \rangle - \langle c_{I\sigma}^{\dagger} a_{n\alpha} \rangle \langle \langle c_{I\sigma} | c_{k+}^{\dagger} \rangle \rangle &= \delta_{\sigma\alpha}. \end{aligned} \quad (2.10)$$

A consequence of the fact that there is no external magnetic field is that the electron spins and the impurity spins have no preferred direction. This means

$$\begin{aligned} (1) \quad \langle S_z^n \rangle &= 0 \\ (2) \quad \langle c_{I+}^{\dagger} c_{I+} \rangle &= \langle c_{I-}^{\dagger} c_{I-} \rangle \end{aligned}$$

which implies

$$\begin{aligned} \sigma_z^n &= 0 \\ (3) \quad \langle a_{n+}^{\dagger} c_{I+} \rangle &= \langle a_{n-}^{\dagger} c_{I-} \rangle \end{aligned}$$

which implies

$$\alpha_n^+ = \alpha_n^- = \alpha_n.$$

So, the self consistent equations for the Green Function for the system with no magnetic field are:-

$$(\omega - \epsilon_k) G_{kk} - \frac{3J}{4N} \sum_{n=1}^2 e^{-ik \cdot R_n} \alpha_n F_{nk} = \frac{\delta_{kk'}}{2\pi} \quad (2.11)$$

$$\omega F_{nk} = \frac{3J}{4N} \bar{\alpha}_n G_{nk} \quad (2.12)$$

and from (2.8)

$$\begin{aligned} \alpha_n &= i \int_{-\infty}^{\infty} d\omega f(\omega) \\ &\times \sum_{\mathbf{k}} (F_{n\mathbf{k}}(\omega + i\delta) - F_{n\mathbf{k}}(\omega - i\delta)) e^{-i\mathbf{k} \cdot \mathbf{R}_n}. \end{aligned} \quad (2.13)$$

3. SOLUTION OF DECOUPLED EQUATIONS

By dividing (2.11) by $(\omega - \epsilon_{\mathbf{k}} \pm i\delta)$, multiplying throughout by $e^{i\mathbf{k} \cdot \mathbf{R}_n}$ and summing over $\mathbf{k}'$ we obtain

$$\begin{aligned} G_{1\mathbf{k}} - \frac{3J}{4N} (\mp \rho \pi i \alpha_1 F_{1\mathbf{k}} + d_2 P_{12}^{\pm} F_{2\mathbf{k}}) \\ = \frac{e^{i\mathbf{k} \cdot \mathbf{R}_1}}{2\pi(\omega - \epsilon_{\mathbf{k}} \pm i\delta)} \end{aligned} \quad (3.1)$$

and a similar equation may be obtained for $G_{2\mathbf{k}}$.

Here, we have made the approximation

$$\sum_{\mathbf{k}} \frac{1}{\omega - \epsilon_{\mathbf{k}} \pm i\delta} = \mp \rho \pi i \quad (3.2)$$

and taken

$$P_{12}^{\pm} = \frac{1}{\rho \pi} \sum_{\mathbf{k}} \frac{e^{i\mathbf{k} \cdot (\mathbf{R}_1 - \mathbf{R}_2)}}{\omega - \epsilon_{\mathbf{k}} \pm i\delta} \quad (3.3)$$

where $\rho(\omega)$ is the density of states and

$$\rho(\omega) \approx \rho(0) \approx \rho$$

$P_{12}^{\pm}$ may be calculated using a free electron model. If k_0 is the momentum corresponding to the energy ω , then, for large separations, R

$$P_{12}^{\pm} = -\frac{e^{\pm i k_0 R}}{k_0 R}. \quad (3.4)$$

Details of this calculation are included in the Appendix, where it is also shown that $P_{12}^{\pm} = P_{12}^{\pm}$. This quantity is henceforth referred to as $P^{\pm}$, the ω dependence being understood.

The solution at (3.1), together with (2.11)-(2.13), involve the introduction of quantities A_n , $n = 1, 2$ which are defined as follows:

$$A_n = \frac{9J^2 \rho \pi}{16N^2} \alpha_n \bar{\alpha}_n, \quad n = 1, 2. \quad (3.5)$$

It may be seen from an examination of a system of an isolated impurity situated away from the origin and the symmetry of this problem that

$$A_1 = A_2 = A. \quad (3.6)$$

The results one obtains are

$$F_{1k}(\omega) = \frac{3J\bar{\alpha}_1}{8\pi N\Delta^\pm} \frac{1}{\omega - \epsilon_k} (e^{i\mathbf{k}\cdot\mathbf{R}_1}(\omega \pm iA) + e^{i\mathbf{k}\cdot\mathbf{R}_2}AP^\pm) \quad (3.7)$$

and a similar equation for F_{2k} and

$$G_{kk}(\omega) = \frac{\delta_{kk}}{2\pi(\omega - \epsilon_k)} + \frac{1}{\rho\pi\Delta^\pm(\omega - \epsilon_k)(\omega - \epsilon_{k'})} \times [A(\omega \pm iA)(e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_1} + e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_2}) + A^2P^\pm(e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_1} + e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_2})] \quad (3.8)$$

where

$$\Delta^\pm = (\omega \pm iA)^2 - A^2(P^\pm)^2.$$

Primarily, we are interested in the relaxation time τ_k which leads to the conductivity. So we require the Green function G_{kk} which is given by

$$2\pi(\omega - \epsilon_k)G_{kk} = 1 + \frac{2A}{\rho\pi} \frac{\Sigma^\pm}{(\omega - \epsilon_k)} \quad (3.9)$$

where

$$\Sigma^\pm = \frac{1}{\Delta^\pm} [(\omega \pm iA) + AP^\pm \cos \mathbf{k} \cdot \mathbf{R}] \quad (3.10)$$

where $\mathbf{R} = \mathbf{R}_2 - \mathbf{R}_1$

each term in $\Sigma^\pm$ is of the order $\left|\frac{J}{N}\right|\rho$ or higher.

Here, we assume $\left|\frac{J}{N}\right|\rho \ll 1$, and, therefore,

$$\frac{G_{kk}^{-1}(\omega \pm i\delta)}{2\pi} = \omega - \epsilon_k - \frac{2A}{\rho\pi} \Sigma^\pm. \quad (3.11)$$

The problem now remaining is to find A .

4. THE INTEGRAL EQUATION FOR A

To this end we must use equation (3.7), which gives F_{1k} , together with equation (2.13) for $\bar{\alpha}_n$.

The subsequent manipulation requires the summation of the series

$$\sum_k e^{-i\mathbf{k}\cdot\mathbf{R}_1} F_{1k}(\omega \pm i\delta) = \frac{3J\rho\bar{\alpha}_1}{8N\Delta^\pm} [\mp i(\omega \pm iA_2) + A(P^\pm)^2]. \quad (4.1)$$

As a result A is determined by

$$1 = \frac{3J\rho}{4N} \int_{-D}^D \frac{\omega f(\omega)}{\Delta^+ \Delta^-} [\omega^2 - A\omega Y + A^2(1 + X)] d\omega \quad (4.2)$$

where

$$X \mp iY = (P^\pm)^2. \quad (4.3)$$

This equation goes over to the form for a single impurity[3] when the impurity separation R , becomes very large.

Equations (3.11) and (4.2) are true for all temperatures and separations. Apart from the usual pole at $\omega = \epsilon_k$, the retarded Green Function (3.11) has two additional poles when $\omega = Ai \pm AP^\pm(\omega)$.

A is essentially a separation dependent form of Nagaoka's Δ and we see that in the region where $P^\pm$ is independent of ω [8], the quasibound state of the single impurity system splits into two, symmetrically spaced either side of the Fermi surface. The energies of the two resonances are $\pm AH$ with corresponding widths $A(1 \pm K)$ where $P^\pm = (H \mp K)$.

The exact separation dependence we obtain for A is not required for the main conclusion of this paper, but it is interesting to notice that when $A = 0$ the additional poles of the Green Function are removed. This condition, therefore, defines T_c , the temperature at which the quasibound states disappear. So, T_c is determined by

$$1 = \frac{3J\rho}{4N} \int_{-D}^D \frac{f(\omega)}{\omega} d\omega \quad (4.4)$$

which is the same result as in the isolated impurity system. Therefore, T_c is independent of R . In a real system of impurities in a metal, this will be reflected in an independence at concentration. This is in agreement with Nagaoka's result[6].

5. THE CONTRIBUTION TO THE CONDUCTIVITY

In working out the effect that two impurities separated by a distance R has on the electrical conductivity, we must make approximations in the Green function. When working out the conductivity from the relaxation time τ_k , we have to integrate over the directions of $\mathbf{k}$. This means that any terms of the form $P^\pm \cos \mathbf{k} \cdot \mathbf{R}$ will result in a factor $1/(k_F R)^2$. Bearing this in mind, we shall expand the Green Function in powers of $1/(k_F R)^2$. The Green Function will give us the relaxation time and hence the conductivity. We expand Σ^+ , which is essentially the self-energy of the retarded Green Function, to first order in X and Y

$$\Sigma^+ = \frac{\omega + Ai + AL}{(\omega + Ai)^2 - (P^+)^2 A^2} \quad (5.1)$$

where

$$L = P^+ \cos \mathbf{R} \cdot \mathbf{k} = L_R + L_I.$$

We now write $A = A_0 + \delta A$ where δA contains all the R and I dependence of A . Retaining only terms of order δA , (5.1) becomes

$$\Sigma^+ = \frac{1}{\omega + iA_0} + \frac{A_0 L - i\delta A}{(\omega + iA_0)^2} + \frac{A_0^2 (P^+)^2}{(\omega + iA_0)^3}. \quad (5.2)$$

Rationalising this expression we obtain

$$\begin{aligned} \Sigma^+ = & \frac{\omega - iA_0}{\omega^2 + A_0^2} + \left[\frac{1}{(\omega^2 + A_0^2)^2} (A_0 L_R (\omega^2 - A_0^2) \right. \\ & + 2A_0^2 \omega L_I - 2\omega A_0 \delta A) + \frac{A_0^2}{(\omega^2 + A_0^2)^3} \\ & \times (X\omega(\omega^2 - 3A_0^2) + A_0 Y(A_0^2 - 3\omega^2)) \Big] \\ & + i \left[\frac{1}{(\omega^2 + A_0^2)^2} (A_0 L_I (\omega^2 - A_0^2) \right. \end{aligned}$$

$$\begin{aligned} & - 2A_0^2 \omega L_R - (\omega^2 - A_0^2) \delta A) + \frac{A_0^2}{(\omega^2 + A_0^2)^3} \\ & \times (A_0 X(A_0^2 - 3\omega^2) - \omega Y(\omega^2 - 3A_0^2)) \Big]. \quad (5.3) \end{aligned}$$

The two impurity relaxation time τ_k is obtained from the imaginary part of the self-energy of the retarded Green Function $G_{kk}(\omega)$

$$\frac{G_{kk}^{-1}(\omega)}{2\pi} = \omega - \epsilon_k - \frac{2A}{\rho\pi} \Sigma^+. \quad (5.4)$$

So we have

$$\begin{aligned} \frac{1}{\tau_k} = & \frac{2A_0}{\rho\pi(\zeta_k^2 + A_0^2)} \left[A_0 + \delta A - ((L_I A_0 - \delta A) \right. \\ & \times (\zeta_k^2 - A_0^2) - 2A_0^2 \zeta_k L_R) \frac{1}{(\zeta_k^2 + A_0^2)} \\ & - \frac{A_0^2}{(\zeta_k^2 + A_0^2)^2} (A_0 X(A_0^2 - 3\zeta_k^2) \\ & \left. - \zeta_k Y(\zeta_k^2 - 3A_0^2)) \right]. \quad (5.5) \end{aligned}$$

Inverting both sides

$$\begin{aligned} \tau_k = & \frac{\rho\pi}{2} \left[\left(\left(\frac{\zeta_k}{A_0} \right)^2 + 1 \right) - \frac{1}{A_0} \left(\delta A \left(\left(\frac{\zeta_k}{A_0} \right)^2 + 1 \right) \right. \right. \\ & - (L_I A_0 - \delta A) \left(\left(\frac{\zeta_k}{A_0} \right)^2 - 1 \right) \\ & + 2\zeta_k L_R - A_0 X \left(\frac{A_0^2 - 3\zeta_k^2}{\zeta_k^2 + A_0^2} \right) \\ & \left. \left. + \zeta_k Y \left(\frac{\zeta_k^2 - 3A_0^2}{\zeta_k^2 + A_0^2} \right) \right) \dots \right] \quad (5.6) \end{aligned}$$

We now calculate the change in the conductivity due to two impurities, $\Delta\sigma$. The formula we use is

$$\Delta\sigma = -\frac{e^2}{12\pi^3} \int \tau_k v_k^2 \frac{\partial f}{\partial \zeta_k} d^3 \mathbf{k}. \quad (5.7)$$

For terms involving R , we may essentially take $-\partial f / \partial \zeta_k$ to be a δ -function.

Using this, together with the integrals

$$\int_{-D}^D \zeta_{\mathbf{k}} \frac{\partial f}{\partial \zeta_{\mathbf{k}}} d\zeta_{\mathbf{k}} = -\frac{\pi^2}{3} T^2, \quad \int_{-D}^D \frac{\partial f}{\partial \zeta_{\mathbf{k}}} d\zeta_{\mathbf{k}} = -1$$

we obtain

$$\Delta\sigma = \frac{ne^2\rho\pi}{2m^*} \left(1 + \frac{\pi^2}{3} \left(\frac{T}{A_0} \right)^2 + H_0^2 + \frac{1}{2} K_0^2 \right) \quad (5.8)$$

where $H_0 = H_{(0)}$ (see Appendix) etc.

This result is true for $(k_F R)^2 \gg 1$.

Hence

$$\rho_{res} = \rho_2 \left(1 - \frac{\pi^2}{3} \left(\frac{T}{A_0} \right)^2 - H_0^2 - \frac{1}{2} K_0^2 \right) \quad (5.9)$$

where $\rho_2 = \frac{2m^*}{ne^2\rho\pi}$ which is the zero temperature resistivity for two isolated impurities, and n is the total number of conduction electrons, and m^* is the effective mass of the conduction electrons[2].

We see that the effect of including the interaction between the impurities due to a finite separation is a reduction in their composite resistivity.

The way H_0 depends on R is shown in Fig. 1.

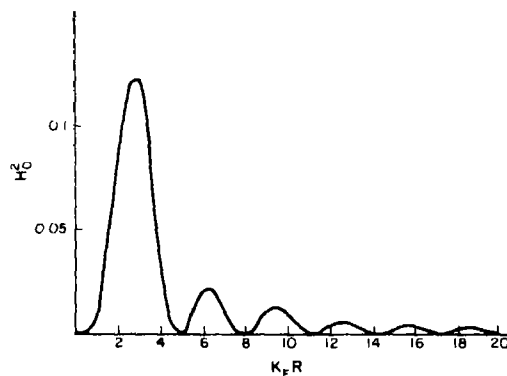


Fig. 1. In the region where we may neglect $\frac{1}{(k_F R)^4}$ ($k_F R \gg 3$) this plot represents part of the reduction in the resistivity due to the interaction between the two impurities divided by the interaction free zero temperature value.

With the more severe condition $k_F R \gg 1$ we may write

$$\rho_{res} = \rho_2 \left(1 - \frac{\pi^2}{3} \left(\frac{T}{A_0} \right)^2 - \rho_{12}(R) \right) \quad (5.10)$$

where

$$\rho_{12} = \frac{\cos^2 k_F R}{(k_F R)^2} + \frac{1}{2(k_F R)^2}. \quad (5.11)$$

6. APPLICATION OF THIS RESULT

Apart from the last term, (5.11) is the same as Nagaoka's result for two isolated impurities. Therefore, $\rho_2 \rho_{12}(R)$ is the reduction in the resistivity due to the co-operative effect between the impurities. To apply this result to the real physical system we must multiply the first part of (5.10) by $nc/2$ to obtain the resistivity of all the impurities as though they were isolated. Then we must subtract from this the co-operative effects of all possible pairings. The latter quantity we call ρ_1 .

Let us start by supposing that ρ_1 may be calculated by summing the two impurity reduction in pairs directly. Suppose the impurities are uniformly distributed and take the origin to be at an impurity site. The number of impurities in a spherical shell of radius R centred on the origin with thickness dR is $\frac{4\pi N_c}{V} R^2 dR$. ρ_1 is then given by

$$\rho_1 = \frac{2\pi (N_c)^2}{V k_F^2} \rho_2 \int (\cos^2 k_F R + 1) dR. \quad (6.1)$$

The multiplying factor of $N_c/2$ must be included to account for other possible pairings. This integral diverges and shows that there must be other important factors involved apart from the two impurity interaction. In the calculation of the resistivity it was assumed that the crystal lattice was perfect. This means that the conduction electrons travel freely and are only scattered by the two magnetic impurities. However, the electrons are also scattered by phonons, displaced ions and other impurities, magnetic or not. To take this into account we

use the concept of the mean free path of the conduction electrons. The integrand of (6.1) must be multiplied by the probability that the electrons can travel undisturbed between impurities separated by a distance R .

If λ is the overall mean free path then the probability of a path length between x and $x + dx$ is

$$\frac{e^{-x/\lambda}}{\lambda} dx. \quad (6.2)$$

Therefore, the probability, $\rho(R)$, that the electrons travel, undisturbed, at least the distance from the origin to shell of radius R is given by.

$$P(R) = e^{-R/\lambda} \quad (6.3)$$

$e^{-R/\lambda}$ is essentially the probability that the conditions of the calculation are fulfilled and (6.1) now becomes

$$P_1 = \frac{\pi(Nc)^2}{V k_F^2} \int e^{-R/\lambda} (\cos^2 k_F R + 1) dR. \quad (6.4)$$

Since $k_F \lambda \gg 1$ the calculation at the integral gives

$$\rho_1 = \frac{3\pi(Nc)^2 \rho_2 \lambda}{2V k_F^2} \quad (6.5)$$

and the final result is

$$\rho_{\text{res}} = \rho_0 \left(1 - \frac{\pi^2}{3} \left(\frac{T}{A_0} \right)^2 - \frac{3\pi N c \lambda}{V k_F^2} \right) \quad (6.6)$$

where

$$\rho_0 = \frac{Nc}{2} \rho_2 \quad (6.7)$$

and the expression for λ is

$$\lambda = \frac{v_F m^* \sigma}{n e^2} \quad (6.8)$$

σ being the conductivity.

The coefficient of c^2 is the expansions of

the resistivity depends only on two particle scattering. In the low temperature region, where the scattering is predominantly magnetic, the resistivity is obtained by adding ρ_{res} to the non-magnetic scattering term ρ_A which also is proportional to c [1]. This means that λ is proportional to $1/c$ and the result is a reduction in the resistivity proportional to c .

At higher temperatures, above the Kondo minimum, the scattering is largely due to phonons and hence λ would be independent at c . However, this is outside the scope of the present work as (5.9) is not valid in this region.

Acknowledgement—One of the authors (T. G.), would like to thank the S.R.C. for financial support.

REFERENCES

1. KONDO J., *Prog. theor. Phys.* **32**, 37 (1964).
2. NAGAOKA Y., *Phys. Rev.* **138**, A1112 (1965).
3. TAKANO F. and OGAWA T., *Prog. theor. Phys.* **35**, 343 (1966).
4. BRESEMANN R. H. and BAILLYN M., *Phys. Rev.* **154**, 471 (1967).
5. BEAL-MONOD M. T., *Phys. Rev.* **178**, 874 (1969).
6. NAGAOKA Y., *J. Phys. Chem. Solids* **27**, 1139 (1966).
7. ZUBOREV D. N., *Usp. Fiz. Nauk* **71**, 71 (1960) [English Translation: *Soviet Phys. Usp.* **3**, 320 (1960)].
8. CAROLI B., *J. Phys. Chem. Solids* **28**, 1427.

APPENDIX

Here, we evaluate $P_{12}^{\pm}$ by first converting it into an energy integral.

The angular integrations are relatively straightforward, and we find

$$P_{12}^{\pm} = \frac{1}{\rho \pi} \int_{-\pi}^{\pi} \frac{\rho(\zeta)}{\omega - \zeta \pm i\delta} \frac{\sin R k_i}{R k_i} d\zeta \quad (A1)$$

$$P_{12}^{\pm} = (H \mp iK)$$

where ζ is the energy of an electron of wave vector k_i and $\rho(\zeta)$ the density of states. We assume a band width of $2D$ centred at the Fermi energy.

By replacing R by $-R$, we see immediately that $P_{12}^{\pm} = P_{21}^{\pm}$. Then, quite simply

$$\rho \pi K(\omega) = \rho(\omega) \pi \frac{\sin k_0 R}{k_0 R} \quad (A2)$$

and

$$\rho \pi H(\omega) = P \int_{-\pi}^{\pi} \frac{\rho(\zeta)}{\omega - \zeta} \frac{\sin k_i R}{k_i R} d\zeta \quad (A3)$$

provided that $-D < \omega < D$.

To evaluate H , we take a free electron model with

$$\zeta_k = \frac{k^2 - k_F^2}{2m} \quad \text{and} \quad \omega = \frac{k_0^2 - k_F^2}{2m}$$

where ζ_k is measured from the Fermi surface.

Making this substitution in (A3) and converting the integral into a more convenient form

$$H(\omega) = \frac{1}{\pi R k_0} \left(\int_{(k_0 - L)R}^{(k_0 + L)R} \frac{\sin(k_0 R - y)}{y} dy + \int_{(k_0 + L)R}^{(k_0 + L)R} \frac{\sin(y - k_0 R)}{y} dy \right) \quad (\text{A4})$$

where

$$U = (k_F + 2mD)^{1/2}$$

$$L = (k_F - 2mD)^{1/2}.$$

The limits of integration on the first integral span zero and on the second both are positive. So for large separations ($k_0 R \gg 1$)

$$H(\omega) = -\frac{\cos k_0 R}{k_0 R} \quad (\text{A5})$$

and

$$P^z(\omega) = \frac{e^{z i k_0 R}}{k_0 R}. \quad (\text{A6})$$

It follows that

$$H_0 = -\frac{\cos k_F R}{k_F R}. \quad (\text{A7})$$

DIRECT OBSERVATION OF IMPURITY MOTION IN QUARTZ USING THE RAMAN EFFECT

R. R. SHARP and E. L. PACE

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106, U.S.A.

(Received 21 January; in revised form 21 May 1969)

Abstract—Intensity enhancements in the Raman spectrum of quartz have been found to occur when crystals are subjected to ultrasonic stress. Negative enhancements having magnitudes up to fifteen per cent of the total band intensity, have been studied in the $466\text{ cm}^{-1}(A_1)$ and $207\text{ cm}^{-1}(A_1)$ modes. Enhancements appear above a threshold in ultrasonic strain amplitude and follow approximately the pattern of strain gradient in the ultrasonic standing wave. These effects are attributed to motion of silver impurities trapped in cylindrical channels of the lattice parallel to the quartz optic axis.

INTRODUCTION

AN INVESTIGATION of the effect of large amplitude ultrasonic stress on the Raman spectrum of quartz has been undertaken in this laboratory. The original object of this study was to determine whether achievable lattice strains are large enough to produce a detectable violation of symmetry selection rules or a measurable broadening of Raman bands due to anharmonic interaction. Neither of these predicted phenomena was of detectable magnitude, although previously recorded spectra[1, 2] in the presence of static stress indicated that broadening, at least, might be present. A number of spectral changes involving primarily intensity enhancements have been observed.

EXPERIMENTAL

The quartz resonators were obtained commercially as rectangular *X*-cut prisms of optical quality, natural quartz. Specimens supplied were optically polished and free of optical and electrical twinning, only right handed samples being used. The prism dimensions and the orientation of crystal axes are shown in Fig. 1. The thickness vibration along *X*, a compressional mode, was excited at fundamental (445 kHz) and third harmonic (1335 kHz) frequencies. Raman spectra of the required intensity were dependent upon

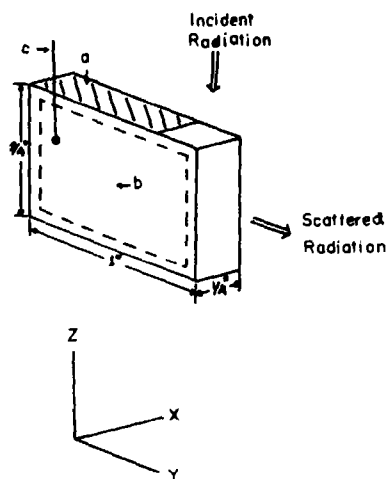


Fig. 1. Quartz transducer.

several laser passes inside the crystal. For efficient internal reflection three edges (a) of each sample were coated with vapor deposited silver. Ultrasonic electrodes (b) were also vapor deposited silver. A small window, $\frac{1}{4} \times \frac{1}{4}$ in., remained uncoated to allow entrance of the laser beam. 38 gage copper lead wires (c), which joined the transducer electrodes to the ultrasonic generating circuit, were connected by conducting epoxy cement. Quartz samples were held in a Teflon holder, which was designed to grip the crystals by

their four short edges without causing excessive ultrasonic damping or blocking of the optical paths into or out of the crystal. The Teflon holder was mounted firmly to a mechanical stage that was situated on an optical track.

Exciting radiation for the Raman spectrometer was obtained from a Perkin-Elmer Model 5300 He-Ne laser, which provided 12 mW of radiant energy at 6328 Å. Scattered light was collected by a condensing achromat, 9.5 cm in dia. by 33 cm focal length, and was focused on the entrance slit of the monochromator. Since the quartz specimens were quite small compared to dimensions of the light collecting system, the efficiency of light collection was approximately maximized by imaging the center of the crystal on the slit. By choosing a suitable magnification it was possible to restrict the region of sample being observed to a narrow slice of crystal approximately 300 μ thick, lying parallel to the crystal YZ plane. Localization of the region of sample observed to a plane of almost constant ultrasonic phase was crucial for the experimental measurements. Planes of sample under observation were perpendicular to the X axis and could be specified by their displacement in inches, or horizontal travel, along the X axis between the two broad crystal faces.

The incident laser beam entered the sample at an inclination of 3–7° from the Z axis. The optical activity of quartz caused the electric vector, which was incident along the X axis in experiments described below, to rotate through 360° several times in the course of being internally reflected in the crystal. Scattered intensity from the totally symmetric bands were found to be uniform along the Z axis demonstrating that the polarization vector had been effectively averaged along this direction.

Scattered light was analyzed by a Spex No. 1700–11 grating monochromator, which consisted of a 0.75 m focal length Czerny–Turner mount in a light-tight housing. The

Raman signal was detected by a photomultiplier and synchronously amplified by a Brower Model 130 amplifier. A beam chopper was placed immediately after the scattering source and provided a reference signal for phase sensitive amplification. Amplified signals were integrated and displayed on a chart recorder. The ultrasonic generating circuit consisted of a Marconi Instruments Model TF 144H Standard Signal Generator followed by a General Radio type 1233-A Power Amplifier. Ultrasonic current passed by the crystal was monitored by the voltage drop across a 10 Ω resistance to ground. Strain amplitude, S_0^0 , at the node of the ultrasonic standing wave is directly proportional to the crystal current, I , in mA:

$$S_0^0 = (1.3)(10^{-5})I.$$

The strain amplitude S^0 at values of horizontal travel, d , other than 0.125 in. is given by

$$S^0 = S_0^0 \sin(\pi d/0.250).$$

EXPERIMENTAL RESULTS

Ultrasonically induced alterations of the Raman spectrum of optical quality quartz were not large enough to permit positive identification. In these measurements crystals were excited to straining amplitudes of $S_0^0 = 4 \times 10^{-5}$ in the fundamental ultrasonic mode. Intense Raman bands at 127 $\text{cm}^{-1}(E)$, 207 $\text{cm}^{-1}(A_1)$, and 466 $\text{cm}^{-1}(A_1)$ were carefully examined for evidence of broadening or intensity enhancements. A small (2 per cent) positive intensity enhancement in the 466 cm^{-1} band appeared to be present but this enhancement was of the order of the experimental uncertainty. Spectral regions near 364 cm^{-1} and 495 cm^{-1} were searched using large slit widths and maximum sensitivity but did not reveal the presence of symmetry forbidden bands.

One quartz sample, which had been heated to the neighborhood of 250°C in order to cure cemented joints between the electrodes and

ultrasonic lead wires, exhibited a remarkably intensified and otherwise altered scattering spectrum. This sample assumed a faint yellow-brown hue and both the Rayleigh and Raman spectra were intensified by a factor approximately of five. The Raman spectrum contained in addition to the intensified spectrum of lattice fundamentals an intense, rather broad band near 200 cm^{-1} . This band was roughly half as intense as the 207 cm^{-1} mode, with which it overlapped.

Band intensities in the heat treated sample (crystal I) were found to vary remarkably in the presence of an ultrasonic stress. Detailed Measurements of these perturbations were obtained only on the 466 cm^{-1} band. As was mentioned above, the spectrometer light collecting system permitted the region of sample from which scattered light was collected efficiently to be localized to a flat slab, approximately 300μ wide, oriented in a plane of constant ultrasonic phase. Vertical regions of this slab could be masked as desired at the entrance slit. The position of the slab in the ultrasonic standing wave was varied by displacing the sample on its mechanical stage parallel to the crystal X axis. The displacement, d , from one crystal face, given in inches, is termed horizontal travel. Scattered intensity, as well as ultrasonically induced intensity enhancements, were uniform along the crystal Z axis except within 1.5 mm of the upper and lower surfaces. The slit was masked to these regions during measurements.

Induced intensity enhancements were measured as a function of strain amplitude and horizontal travel. Typical measurements consisted of sitting on the band center and switching on ultrasonic power in three bursts of approximately two minutes duration. Data points are thus averaged over at least six readings, the average deviation being ± 0.3 per cent of the total band intensity. Enhancements under these conditions were always negative (positive enhancements were observed under somewhat different conditions [3]). In the fundamental ultrasonic mode,

enhancements vary with horizontal travel in the unexpected manner exhibited in Fig. 2. Enhancements are roughly proportional to strain gradient (rather than strain) except near the crystal faces where they fall abruptly to zero. A sharp negative peak is seen near $d = 0.214\text{ in.}$ The width of this feature is a good measure of the spectrometer's ability to resolve neighboring regions of sample.

The variation of enhancement with strain amplitude is reproduced in Figs. 3 and 4

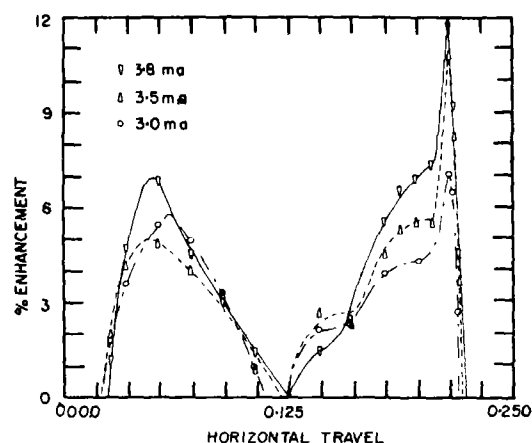


Fig. 2. Variation of Raman negative enhancement with horizontal travel.

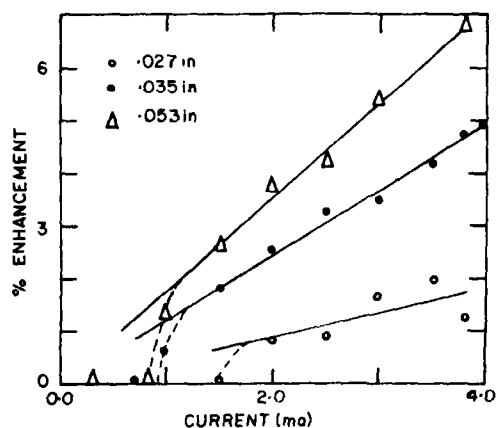


Fig. 3. Variation of Raman negative enhancement with transducer current. Fundamental ultrasonic mode.

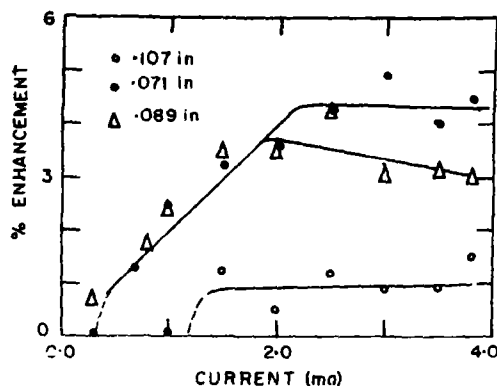


Fig. 4. Variation of Raman negative enhancement with transducer current. Fundamental ultrasonic mode.

for several values of horizontal travel. Measureable enhancements usually occur only above a clearly defined threshold of strain amplitude. This threshold is not constant for different values of the horizontal travel d and does not seem to vary in a simple manner with the ultrasonic standing wave. For example, the threshold strain amplitude is maximized near $d = 0.188$ in. yet virtually disappears at $d = 0.089$ in. although both these positions are at similar locations in the standing wave. Near the crystal center ($d = 0.125$ in.) and the YZ faces ($d = 0.000$ in. and 0.250 in.) enhancements are zero for all measured strain amplitudes. When $d = 0.027$ in., 0.035 in. and 0.053 in., enhancements rise linearly with S^0 when S^0 is above the threshold value. Between 0.089 in. and 0.107 in., the linear region is followed by a 'saturation' value of S^0 , beyond which value enhancements remain roughly constant, or even decrease slightly, with increasing S^0 . The maximum obtainable enhancement (i.e. the value at saturation) decreases progressively as d approaches 0.125 in. Thus the linear region dominates near the crystal faces but is masked by saturation near the center. Between 0.143 in. and 0.179 in. enhancements follow approximately the pattern described for the region between 0.107 in. and 0.089 in. Near the

'anomalous' peak at $d = 0.214$ in. however, enhancements are not linear and do not reach a saturation value. In this region, enhancements exhibit a threshold strain amplitude, above which they vary as the n th power of strain amplitude where n progressively increases with d from about one (at 0.179 in.) to just over two (at 0.214 in.).

A few measurements of enhancement as a function of horizontal travel and strain amplitude were taken at the third harmonic ultrasonic frequency (Fig. 5). The pattern of

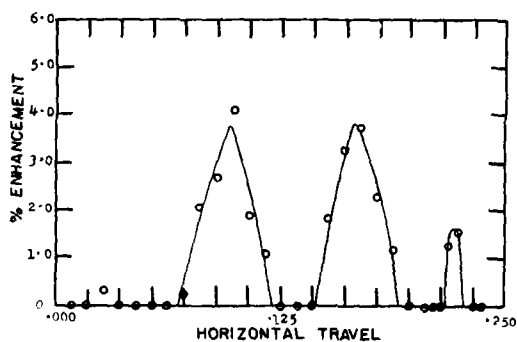


Fig. 5. Variation of Raman negative enhancement with horizontal travel. Third harmonic. Crystal current = 2 mA.

enhancement clearly follows the pattern of strain gradient except near the crystal faces where once again enhancements are zero. Enhancements were approximately a linear function of strain amplitude although scatter in these data was relatively large. Thresholds in strain amplitude were not observed at 1335 kHz.

The patterns of enhancement in this sample were reproducible from day to day and after realignment of the optical system. A few observations that were made on the 207 cm^{-1} band showed identical results to measurements on the 466 cm^{-1} band. Polarization studies on the enhanced bands showed that the totally polarized $466\text{ cm}^{-1}(A_1)$ band remained totally polarized when enhanced. A second sample, which had previously shown a normal and nonenhanceable Raman

spectrum, was heated to the neighborhood of 150°C in an attempt to reproduce the effects described above. The heat treatment did produce intensified Raman and Rayleigh scattering as well as a yellow-brown hue similar to that observed in crystal I. Negative enhancements, clearly associated with thresholds, were likewise induced in crystal II, although the detailed pattern of enhancement with changing strain and horizontal travel differed significantly in the two samples. Further details of these measurements are given in Ref. [3].

DISCUSSION

The foregoing experimental observations clearly indicate that Raman enhancements are not a property of the intrinsic quartz lattice, but rather result from lattice defects that are created when quartz is heated in contact with surface coatings of metallic silver. The introduction of impurity ions into single crystals of quartz at elevated temperature was first discovered and interpreted by Curie[4] and has since been well characterized in conductance and ultrasonic decrement experiments [5, 6, 7]. Metallic migration occurs preferentially along the quartz optic axis as a result of open channels in the lattice structure. A faint brown hue accompanies the introduction of these ions into the lattice[6]. The very strikingly intensified Rayleigh scattering observed in defect containing samples is quite probably due to the large polarizabilities of heavy impurity atoms. The marked intensification of lattice fundamentals in the Raman

spectrum is rather surprising, however, and should probably be ascribed to highly diffuse impurity wave functions which extend far enough into the quartz lattice to couple with the intrinsic modes. The single extraneous spectral feature (a broad band near 200 cm^{-1}) is tentatively assigned as an impurity band.

The preliminary results so far obtained are not sufficiently detailed to show clearly the mechanism by which wave functions of the silver impurities couple with an ultrasonic vibration. One straightforward explanation of this coupling, which is that the electronic polarizability depends directly upon the degree of lattice strain, is not viable since enhancements are minimized, rather than maximized, at nodes of the ultrasonic wave. The dependence of enhancement upon strain gradient suggests, rather, that mass transport of impurities down the gradient may be involved. Two indirect models of coupling have been found[3] to provide a semi-quantitative explanation of several unusual features in the data.

REFERENCES

1. MARIEÉ M. and MATHIEU J. P., *Compt. Rend.* **223**, 147 (1946).
2. ZUBOV V. G. et al., *Soviet Phys. Crystallogr.* **6**, 623 (1961).
3. SHARP R. R., Ultrasonically Induced Enhancements in the Raman Spectrum of Quartz, Ph.D. Thesis, Case Western Reserve University (1968).
4. CURIE J., *Annls. Chim. Phys.* **18**, 203 (1889).
5. GIBSON G. and VOGEL R. C., *J. chem. Phys.* **18**, 1094 (1950).
6. COOK R. K. and BRECKENRIDGE R. G., *Phys. Rev.* **92**, 1419 (1953).
7. COOK R. K. and WASILIK J. H. *J. appl. Phys.* **27**, 836 (1956).

EFFECT OF DILATION ON THE KNIGHT SHIFT IN LIQUID ALLOYS*

N. C. HALDER

Department of Physics, State University of New York, Albany, N.Y. 12203, U.S.A.

(Received 6 August 1969; in revised form 12 May 1970)

Abstract—A formalism based on the atomic distribution function and phase shift has been applied to a number of liquid alloys at different solute concentrations, and the fractional change of the Knight shift, $\Delta S/S$, of In atom in dilute liquid In-Hg, In-Ga, In-Tl, In-Pb and In-Sn alloys has been determined. The main contributions of this paper are, (a) an introduction of a simple method based on the isotropic-homogeneous-model of the fluid to account for the structural change of the solvent surrounding with added solute concentration, (b) an evaluation of the phase shifts for *s*-, *p*- and *d*-electron scattering appropriate to the conditions set up in a given solvent, and (c) a critical testing of the Odle-Flynn theory for the Knight shift in dilute liquid alloys. The initial slopes, I' , of the plots between $\Delta S/S$ and the solute concentration, are in reasonable agreement with the recent experimental results. For example, $I'(\text{exp})/I'(\text{the})$ is about 1.2, suggesting a remarkable improvement over the previous estimates.

1. INTRODUCTION

SOME experimental measurements[1,2] of the nuclear spin relaxation rates and nuclear magnetic resonance shifts in liquid metals and alloys indicate that the leading term in the Hamiltonian of the nuclear-electron interaction is the Fermi contact term which results from the hyperfine interactions between the two spins. This evidence has, naturally therefore, compelled us to believe that any changes of the magnitudes in relaxation time and Knight shift with temperature, pressure or concentration should predominantly be governed by the factors contained in the Fermi contact term. These factors are the spin paramagnetic susceptibility and the conduction electron density at a given nuclear site. However, in considering the fractional change of the Knight shift with concentration in dilute liquid alloys, one is, to a reasonably good approximation, concerned with the variation of the conduction electron density which depends on the structure of the alloy or the atomic distribution functions. The spin paramagnetic

susceptibility variation for dilute alloys may be considered to be small compared to the spin density variation.

The electron transport and nuclear magnetic properties in a liquid alloy are sensitive to the partial structures formed by all possible pair combinations of the two atomic species. The character of the individual atom and the volume dilation as a result of alloying are expected to exert a substantial influence to these partial structures. In this paper we will show how a structural change caused mainly by the volume dilation can be related to the fractional change of the Knight shift in liquid alloys. In turn, we will examine the extent of validity of the theory of Knight shift that makes use of the atomic distribution functions. We will begin with a formal introduction of the alloy theory.

2. ATOMIC DISTRIBUTION FUNCTIONS IN LIQUID ALLOYS

The radial density function $\rho(r)$ in liquid alloys actually represents the pair probability function of finding a solvent atom at distances between r and $r+dr$ from any reference atom[3]. This function is affected, although by a very small amount, when some impurity atom is dissolved into the pure solvent matrix.

*This work was supported by the Research Foundation of State University of New York and Office of Naval Research.

For solid metals or solutions, one immediately recognizes that

$$\rho(\mathbf{r}) = \sum_n \delta(\mathbf{r} - \mathbf{r}_n) \quad (2.1)$$

where the summation extends over all the lattice points. The δ -function is zero except at the Bragg points. In liquids, however, $\rho(\mathbf{r})$ is continuous and approaches the average density ρ_0 of the liquid at large values of r . Then, $4\pi r^2 \rho(r)$ is the radial distribution function (RDF), the position of the first peak of which gives the average distance between the nearest neighbors.

Let us now denote the radial density function as $\rho_{ij}(r)$, because we have three partial distribution functions in a liquid binary alloy; the subscripts i and j stand for the solvent and solute atoms respectively. The explicit form of the alloy or the total radial density function is [4]

$$\rho(r) = \sum_i \sum_j c_i f_i f_j \rho_{ij}(r) / \langle f \rangle^2, \quad (2.2)$$

in which f_i and f_j are the usual atomic scattering factors and c_i is the atomic concentration of the solvent. After some rearrangements the above equation results in

$$\rho(r) = \left(\frac{w_i^2}{c_i} \right) \rho_{ii}(r) + \frac{2w_i w_j}{c_j} \rho_{ij}(r) + \left(\frac{w_j^2}{c_j} \right) \rho_{jj}(r),$$

where the weighting factors are defined by

$$w_i = c_i f_i / \langle f \rangle.$$

For randomly distributed atoms, a considerable simplification of the above equation occurs because all $\rho_{ij}(r)/c_j$ are then equal; clearly, for dilute alloys it yields $\rho_{ii} \approx \rho(r)$. If we write

$$\rho_i(r) = \rho_{ii}(r)/c_i,$$

and

$$\rho_j(r) = \rho_{jj}(r)/c_j,$$

it is easy to see

$$\rho_i(r) = (1/w_i^2) \rho(r) - (2w_j/w_i) \rho_{ij}(r)/c_j - (w_j/w_i)^2 \rho_j(r). \quad (2.3)$$

Thus we see that the density function which one uses in the pure liquid metal case should be replaced by $\rho_i(r)$, as stated in equation (2.3), for a liquid alloy. It is apparent that we need $\rho(r)$, $\rho_{ij}(r)$ and $\rho_j(r)$ to determine $\rho_i(r)$. As pointed out earlier [3, 4], in general, these three functions are not known and an experimental measurement of them is not easily accessible, we are forced to rely on some kind of theoretical model. One such reasonably good model is the homogeneous-isotropic-model, which includes the volume dilation around the impurity. This was suggested by Faber and Ziman [5] in the calculation of the electron transport properties of liquid alloys, and proved to be successful in the calculation of the Knight shift from the pseudopotential formalism.

Let us assume that the introduction of any solute atom produces only a slight change from the structure of the pure solvent. Next, we consider that a solvent atom is replaced by a solute atom as a result of which the neighboring atom suffers a shift from the position r to r' . This means that the radial density changes from $\rho(r)$ to $\rho_i(r)$. We express the dilation as

$$\delta_0 = (\Omega' - \Omega) / \bar{\Omega}. \quad (2.4)$$

where Ω' and Ω are the atomic volume of the element in presence and absence of the impurity atom respectively, and $\bar{\Omega}$ is the mean atomic volume. Then a treatment for a homogeneous-isotropic-medium shows that the average change in radial distance of any atom will be

$$\Delta r = r' - r = (\Omega' - \Omega) / (4\pi r^2). \quad (2.5)$$

If we neglect the composition or density fluctuation in the liquids, to a good approximation we may write

$$\rho_i(r) = \rho(r - \Delta r).$$

We can expand it by Taylor's series assuming

that $\rho(r)$ possesses derivatives of all orders in intervals of Δr , and obtain

$$\rho_i(r) = \rho(r) + \frac{d\rho(r)}{dr}(-\Delta r) + \frac{d^2\rho(r)}{dr^2}\frac{(-\Delta r)^2}{2!} + \dots + \frac{d^n\rho(r)}{dr^n}\frac{(-\Delta r)^n}{n!} + \dots \quad (2.6)$$

This equation is much simpler than equation (2.3), and may be viewed as a substitute to overcome the practical difficulties. However, in practice the terms beyond the second derivative are negligibly small and, therefore, may be dropped.

The problem which we have discussed above, may also be handled by an alternative procedure which is mathematically more rigorous. This is the hard-sphere-model calculation of the partial interference functions as suggested by Ashcroft and Lekner[6]. By now it has become quite certain that the hard-sphere-model does not work in the case of liquid Hg, Ga and Sn which we are interested in at present. Attempts to calculate the interference functions for these metals with the various packing densities and the hard-sphere-diameters, were unsuccessful. That is to say, the asymmetry in the first peak of the interference functions towards the short wavelength, as observed experimentally, could not be produced with the hard-sphere-model. In view of this, the hard-sphere-model was rejected from any considerations here.

3. NUCLEAR MAGNETIC RESONANCE IN LIQUID ALLOYS

(a) *Some general remarks on Knight shifts*

A number of mechanisms has been proposed[8-12] to understand the sign and size of the change in the Knight shift in liquid alloys that are generally characterized by the ionic behavior of the dissolved ion, the actual valence of the solute, the magnetic properties of the solute, etc. Since the Knight shifts are attributed to the modifications of the hyperfine interactions by the change in

the electron density of the conduction electrons at the Fermi surface, the most obvious attempt in explaining the Knight shift has come from the nearly-free-electron (NFE) model[13]. The two approaches that are followed in determining the density of the conduction electrons at the Fermi surface are the pseudopotential formalism[14] and the partial wave phase shifts[15]. In general, the theoretical calculations of all the pseudopotentials or the phase shifts are done under some unavoidable approximations which seem to have raised questions; for this reason no unique values of the pseudopotentials or the phase shifts are available[16-19]. Hence a calculation of the Knight shift using these data, will perhaps be subject to the corrections in accordance with our improved understanding on the values of pseudopotentials.

Within the NFE model we will require two quantities, the electron-ion potential and the ion-ion distribution function, to describe the Knight shift in liquid alloys. As pointed out earlier, the former is obtained from a theoretical work and the latter from an elastic scattering experiment. A theoretical computation of the distribution function is also sometimes possible. Usually, one measures the interference function in the momentum space, a Fourier transform of which gives the ion-ion distribution function in the coordinate space.

In two earlier papers[20,21] we have demonstrated that the Knight shift can be qualitatively predicted from the pseudopotential formalism using the interference functions, and emphasized that the NFE model works well both in liquid metals and alloys. Furthermore, it should be noted that in those papers the atomic potentials representing the interactions between the electrons and the ions were considered in the momentum space. In the present text we shall investigate the property of the structure in the coordinate space, i.e., RDF and use directly the atomic potentials. Finally, we shall attempt to evaluate the applicability of the phase shift method and understand

the superiority of the one method over the other in studying liquid alloys. We, therefore, start out with a brief discussion on the theory of the Knight shift involving the phase shift of the impurity atoms and then show how it can be applied to calculate the Knight shift in liquid alloys over somewhat larger composition range.

(b) *Odle-Flynn theory for liquid alloys*

When an impurity is dissolved in a pure metal, the conduction electron gas becomes distorted around the impurity to screen the excess charge. The distortions or oscillations of the electron density, around the impurity atoms produce spherical waves which may introduce effects at large distances. Assuming a spherically symmetric scattering center, Blandin and Daniel[15] developed an equation for the fractional change of the Knight shift in terms of the phase shifts η_l of the impurity atom,

$$\Delta S(r_n)/S(r_n) = \sum_l (2l+1) \{ \{ (n_l^2(kr_n) - j_l^2(kr_n)) \} \sin^2 \eta_l - n_l(kr_n) j_l \times (kr_n) \sin 2\eta_l \}. \quad (3.1)$$

For the phase shifts data, Daniel[22] chose a square well perturbing potential that did not extend beyond the atomic sphere of the impurity atom. Despite the simple nature of the potential and somewhat less sophisticated theory, the above equation gave a fair description of the change of the Knight shift in dilute solid solutions.

Odle and Flynn extended the above theory to investigate the problem of dilute liquid alloys incorporating some modifications due to the short range periodicity of the atomic arrangement and the weak scattering potential in liquids. The Odle and Flynn[8] theory works well for dilute liquid alloys and when the radial density and the phase shift data are available with sufficient accuracy. Rigney and Flynn[9] computed the fractional change of the Knight shift in liquid alloys where they have used a model RDF constructed

from a parabola which was weighted by a pair of δ -functions and cut off in the region of small r . The RDF computed in this way are quite arbitrary and do not give the actual atomic distribution functions in liquids.

(c) *The case of dilated alloys*

It has been mentioned before that the three radial density functions characteristic of the atomic structure and atomic abundance of the two elements are quite important in liquid alloys. This consideration is the key issue here and, in principle, will enable us to investigate the liquid alloys over larger composition range than hitherto been attempted. We can, therefore, introduce a considerable amount of improvement on the Odle-Flynn[8] theory when (1) replacing their average distribution function by the proper elemental $\rho_l(r)$ as shown in equation (2.6), and (2) using η_l for the impurity ions corrected for the changes in volume and screening charges. Such an approach, we believe, is definitely superior over the previous work, and has never been mentioned in the literature. Dealing with the correction on $\rho(r)$ is rather simple and straightforward compared to the other correction on η_l . We shall now concentrate ourselves on these two factors, and proceed to write down a working equation for the dilute liquid alloys.

We consider in dilute alloys that the scattering centers are rather isolated and therefore the interference effects between the solute atoms are unimportant. However, we should take the average effect over all the solvent ions which are surrounding a particular solute; one way of doing this, for example in solids, would be to select a δ -function coupling between different centers:

$$\Delta S/S = \sum_n c_j \frac{\Delta S(\mathbf{r}-\mathbf{r}_n)}{S(\mathbf{r}-\mathbf{r}_n)} \delta(\mathbf{r}-\mathbf{r}_n). \quad (3.2)$$

As indicated in the earlier discussion this δ -function for liquids ought to be replaced

by the radial density function, we may write here,

$$\Delta S/S = \int c_j \frac{\Delta S(\mathbf{r}-\mathbf{r}_n)}{S(\mathbf{r}-\mathbf{r}_n)} \rho_i(\mathbf{r}-\mathbf{r}_n) d^3r, \quad (3.3)$$

where $\rho_i(\mathbf{r}-\mathbf{r}_n)$ is the radial density of the given atom at a distance $|\mathbf{r}-\mathbf{r}_n|$ from the reference atom, whose Knight shift is desired. From the phase shift calculation it can be further shown by an analogous treatment to what has been illustrated in Ref. [15],

$$\Delta S/S = \sum_j c_j [A_l \sin^2 \eta_l + B_l \sin 2\eta_l], \quad (3.4)$$

where

$$A_l = (2l+1) \int_0^\infty \left[\left(\frac{1}{w_l} \right)^2 \rho(r) - \left(\frac{2w_l}{w_l} \right) \rho_{ij}(r)/c_j - \left(\frac{w_l}{w_l} \right)^2 \rho_i(r) \right] [n_l^2(kr) - j_l^2(kr)] d^3r, \quad (3.5)$$

and

$$B_l = -(2l+1) \int_0^\infty \left[\left(\frac{1}{w_l} \right)^2 \rho(r) - \left(\frac{2w_l}{w_l} \right) \rho_{ij}(r)/c_j - \left(\frac{w_l}{w_l} \right)^2 \rho_i(r) \right] [n_l(kr) j_l(kr)] d^3r. \quad (3.6)$$

The weighting factors w_i and radial density functions $\rho_i(r)$ are explicitly defined elsewhere[3]. It is thus evident from the form of the above equations that the fractional change of the Knight shift now should be a complicated function of the atomic concentration. The final trend of the plot between $\Delta S/S$ and concentration is, of course, determined by the extent and sign to which the phase shifts can influence equation (3.4) for various impurities.

Blatt[23] has calculated η_l for a number of atoms using Cu and Ag as solvents. He used a square well potential and varied its range until the Friedel[24] sum rule was

$$\sum_{l=0}^{\infty} (2l+1) \eta_l = \frac{\pi}{2} (Z_j - Z_i), \quad (3.7)$$

satisfied where Z_j and Z_i are the valences of the solute and solvent respectively. Kohn

and Vosko[25] have also computed η_l directly from the electrical resistivity data assuming that the residual electrical resistivity in dilute alloys is proportional to the scattering cross section of the electrons. This is an empirical method limited to very dilute alloys only, and differs drastically from the method of Blatt. Recently Meyer *et al.*[26], have used the pseudoatom concept and obtained η_l as a function of the momentum vector. Thornton and Young[27] showed that the effective phase shift of a pseudoatom can be written as

$$\gamma_l = \eta_l^j - \eta_l^i. \quad (3.8)$$

We see at once that some consideration has been given in this work to incorporate the effect of the solute surroundings because the available pseudopotentials (see Animalu and Heine[28]) are formulated for the neutral pseudoatoms. Faber[29] has shown that a correction due to the dilation corresponding to the changing impurity concentration must be applied to the pseudopotentials which are involved in the scattering of electrons. In view of the importance of this correction factor, we shall illustrate a procedure to account for this effect in the next section.

4. PSEUDOATOM PHASE SHIFTS

The differential scattering cross section for a spherically symmetric potential $V(r)$ of the elastically scattered particles is[30]

$$\sigma(\theta) = \frac{1}{4k^2} \left| \sum_{l=0}^{\infty} (2l+1) P_l(\cos \theta) [e^{-2i\eta_l} - 1] \right|^2$$

or

$$\sigma(\theta) = \frac{1}{k^2} \left[\sum_{l=0}^{\infty} (2l+1) P_l(\cos \theta) \sin \eta_l \right]^2. \quad (4.1)$$

This is an exact result and valid for self-consistent potential which an electron actually sees during the process of scattering. An expansion of the wave function in terms of the plane waves requires a large number of plane waves with nonvanishing coefficients to give a reasonable description of the scattered

wave. In general, a solution of such an equation is extremely difficult. However, in the perturbation treatment, the problem is reduced to 2 or 3 plane-wave-case, i.e., $l = 0, 1, 2$, and can be solved with a reasonable success provided, of course, the s -, p - and d -electron scattering phase shifts are known. An alternative way to get around the solution has been suggested from the orthogonalized plane wave (OPW) treatment[31]. The idea in the OPW method is that the conduction band state must be orthogonal to the core states; this will then give much less terms in the expansion of the wave function and, therefore, the matrix elements in OPW can be calculated more conveniently than in the plane wave. Our aim, at present, is not to describe the OPW method itself but show how we can obtain a solution from it for the scattered wave function in terms of the various matrix elements. At this point we need to introduce the pseudowave function and the pseudopotential.

The pseudopotential $U(\mathbf{r})$ is related to the self-consistent potential $V(\mathbf{r})$ by

$$U(\mathbf{r}) = V(\mathbf{r}) + \sum_{\alpha} (E_k - E_{\alpha}) |\alpha\rangle \langle \alpha|, \quad (4.2)$$

where the energy with the index k and α respectively correspond to the conduction band $|\mathbf{k}\rangle$ and core state $|\alpha\rangle$. Furthermore, the pseudowave functions ϕ_k satisfies the equation

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + U(\mathbf{r}) \right] \phi_k = E_k \phi_k. \quad (4.3)$$

The differential scattering cross section according to the pseudopotential theory for the free electrons impinging on the atom is

$$\sigma(\theta) = \frac{4\pi^2 m^2}{h^4} \left| \int e^{i\mathbf{K} \cdot (\mathbf{r} - \mathbf{r}_n)} u(\mathbf{r} - \mathbf{r}_n) d^3r \right|^2 \quad (4.4)$$

in which we have written $U(\mathbf{r}) = \sum_n u(\mathbf{r} - \mathbf{r}_n)$, and the scattering vector $\mathbf{K} = \mathbf{k}' - \mathbf{k}$. If there are Z free electrons per atom, the above

result becomes

$$\sigma(\theta) = \frac{4\pi^2 m^2}{h^4} \left| \frac{u(\mathbf{K})}{Z\rho_0} \right|^2. \quad (4.5)$$

The matrix elements can then be expressed as

$$u(\mathbf{K}) = \frac{N}{\Omega} \int e^{i\mathbf{K} \cdot (\mathbf{r} - \mathbf{r}_n)} u(\mathbf{r} - \mathbf{r}_n) d^3r \quad (4.6)$$

in which the atomic density N/Ω has been inserted for ρ_0 .

In the above mentioned discussions we have written down the differential scattering cross section for a free electron in two different forms, equations (4.1) and (4.5) which are seen to be quite independent of each other. Now the question arises, are these two cross sections equivalent or do they lead to the same answer when applied to the same dynamical problem? Green and Kohn[32] pointed out that the matrix element $u(\mathbf{K})$ is equivalent to the scattering amplitude of the ion, and may be written in terms of a few partial phase shifts. In fact, they suggested a calculation of the electrical resistivity in liquid metals treating the phase shifts as adjustable variables to obtain the $u(\mathbf{K})$. We will emphasize here the impact of this work and advance a basis for the evaluation of pseudoatom phase shifts.

The work of Green and Kohn[32] may be justified if we recognize that the primary condition in using the perturbation theory is that the potential energy of the perturbed electron must be small compared to the kinetic energy of the scattered electron. This is essentially the Born approximation and has been utilized in arriving at equation (4.5). It is not difficult to see from the foregoing arguments that under this approximation only a few partial waves is required in equation (4.1); we shall see later that only η_l which have $l \leq 2$, are important for our purpose. Therefore, we may now obtain

$$\sum_{l=0}^{\infty} (2l+1) \sin \eta_l P_l \left(1 - \frac{K^2}{2k_F^2} \right) = -\frac{\pi}{2} \left[\frac{u(\mathbf{K})}{\frac{2}{3} E_F} \right], \quad (4.7)$$

where the arbitrary momentum k has been replaced by the Fermi momentum k_F and the normalized $u(K)$ has a value $(-\frac{2}{3})E_F$ at $K = 0$. The most important case of our result is to be noted when $K = 0$, which leads us to the following sum rule

$$\sum_{l=0}^{\infty} (2l+1) \sin \eta_l = \frac{\pi}{2}. \quad (4.8)$$

This result is independent of K and valid as long as we are permitted to adopt the Born approximation. A further reduction of equation (4.2) seems to be in order, provided we choose to employ some well established scattering potentials such as Ascroft's [33] phenomenological form factors,

$$u(x) = -\lambda_0^2 \cos(sx) / [x^2 + \lambda_0^2 f(x)], \quad (4.9)$$

where $x = K/2k_F$, $s = 2k_F R_c$ and $\lambda_0^2 = 1/(\pi a_0 k_F)$. In the above, R_c is the core radius, a_0 is the first Bohr radius and $f(x)$ is the Lindhard dielectric function. Finally, we must insert into it the correction factor due to the effect of dilation and get

$$u'_j(K) = u_j(K) - u_l(K) \delta_0 F(K), \quad (4.10)$$

where $u'_j(K)$ is the effective solute matrix element, and $F(K)$ is the same as used in Ref. [20]. An alternative but simpler procedure would be to use directly the Animalu and Heine $u_j(K)$ and correct them according to the above. We rewrite equation (4.7) to read

$$\sum_{l=0}^{\infty} (2l+1) \sin \eta_l P_l \left(1 - \frac{K^2}{2k_F^2}\right) = -\frac{\pi}{2} \left[\frac{u'_j(K)}{u'_j(0)} \right]. \quad (4.11)$$

For repulsive potentials the negative sign on the right hand side should be dropped and its consequence in the sum rule should be included. It is now quite clear that an effort can be made to compute η_l for s -, p - and d -electrons when three sets of $u(K)$ are available.

5. NUMERICAL COMPUTATIONS FOR DILUTE LIQUID IN-ALLOYS

In this section we present some results obtained using the theories as illustrated in the previous sections. We calculated the phase shift of Hg, Ga, Tl, Pb and Sn and then the Knight shift of the solvent In atom in presence of these polyvalent impurities. We were motivated to study In because its experimental Knight shift data in these alloys are known with certainty [34, 35]. Furthermore, very careful measurements of the radial density functions of the above elements have been also made [20]. In view of this, we expect that a meaningful conclusion regarding the basic idea outlined in this paper can be drawn from the present study.

(a) The computation of the phase shifts

Figure 1 shows the plots of the RDF and the interference function

$$I(K) = 1 + \int_0^{\infty} [\rho(r) - \rho_0] \frac{\sin Kr}{Kr} d^3r, \quad (5.1)$$

for liquid In near the melting temperature. The phase shifts have been calculated with their effective $u(K)$, where the function $F(K)$ was obtained from

$$F(K) = \frac{1}{\rho_0} \int_0^{\infty} \frac{d\rho(r)}{dr} \frac{\sin Kr}{Kr} dr. \quad (5.2)$$

This result asserts that one must know the first derivative of the solute radial density function. In determining η_l we used the Animalu and Heine $u(K)$ and corrected them for the dilation effect. For the sake of brevity two suitable values of $u(K)$, i.e., one at $K = k_F$ and the other at $K = 2k_F$, were selected. Then the requirement was to satisfy the sum rule as stated in equation (4.8). It is often time consuming and less rewarding to generate the function $F(K)$ for all K and then pick out from it the values at k_F and $2k_F$. It would therefore be of great help if we could do some simplifications here and avoid the task of computing. One may easily note that $F(0) = 1$, since the radial density

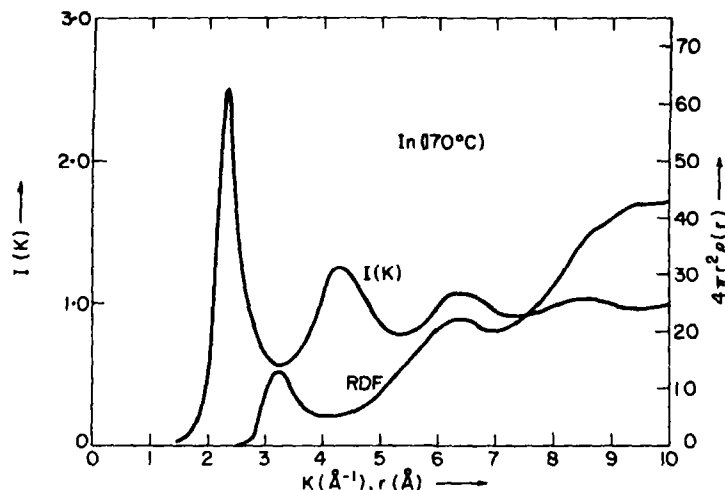


Fig. 1. The plots of interference function $I(K)$ and the radial distribution function RDF for In (170°C). The RDF were obtained from

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^\infty K [I(K) - 1] \sin Kr dK.$$

of atoms at large distances turn out to be the average density of the liquid itself. Also from our experiences with the function $F(K)$ we know that $F(2k_F) \approx 0.3$ and $F(k_F) \approx -0.3$ for the liquid metals under study. These informations produce a considerable amount of easiness and make an absolute determination of η_l possible. However, the best values of η_l can be found from a least square analysis with a series of $u(K)$ values below the Fermi diameter. In this way one may make a full use of both $F(K)$ and $u(K)$. But the outcome is not expected to improve the quality of physics involved here, since a certain amount of uncertainty is always present in any given pseudopotentials and that the η_l are not strongly sensitive to small changes in $u(K)$.

Table 1 shows the values of η_l . These values are a little different from those reported by other workers [23, 25, 37]. As evident here the d -electron scattering is sufficiently small which justifies our application of the Born approximation when a rapid convergence of the series in equation (3.4) is sought. One thing which is quite clear from this result is that γ_l changes smoothly with

increasing solute composition. This change which is perhaps small compared to the other effect, such as, core polarization, spin paramagnetic susceptibility which might occur, is a measure of dilation. We might point out here that this is by no means a unique way of getting appropriate η_l . It is reasonable to say however that the present approach demonstrates a pseudopotential method which includes the atomic distributions.

(b) *The behavior of the coefficients A_l and B_l*

The exact determination of the effective values of the coefficients A_l and B_l presents a problem because these coefficients are not the simple functions of the atomic concentration and the atomic structure. The magnitudes of these coefficients change with the order l and also with the solute concentration. Now the question arises: what values of A_l and B_l should one use? We think this point deserves a mention and must be clearly dealt with.

The integrals of A_l and B_l have the limits ranging from 0 to ∞ , which demand an accurate knowledge of $\rho(r)$ out to very large value of r . We were then tempted to do some com-

Table 1. Phase shifts of the solute atoms in presence of the solvent In atom

Solute %	Hg	Tl	η_0	Ga	Pb	Sn
10	0.5205	-0.5237	0.3436	-0.4329	0.3426	
20	0.5155	-0.5299	0.3401	-0.4383	0.3433	
30	0.5094	-0.5355	0.3366	-0.4433	0.3440	
50	0.5014	-0.5454	0.3294	-0.4523	0.3453	
70	0.4954	-0.5540	0.3219	-0.4602	0.3467	
80	0.4928	-0.5579	0.3181	-0.4639	0.3473	
90	0.4906	-0.5615	0.3142	-0.4673	0.3481	
		η_1				
10	0.3110	-0.2903	0.3101	-0.2942	0.2971	
20	0.3105	-0.2905	0.3094	-0.2954	0.2972	
30	0.3100	-0.2907	0.3087	-0.2948	0.2972	
50	0.3093	-0.2910	0.3073	-0.2954	0.2974	
70	0.3087	-0.2913	0.3058	-0.2958	0.2976	
80	0.3085	-0.2914	0.3050	-0.2961	0.2976	
90	0.3083	-0.2915	0.3042	-0.2963	0.2977	
		η_2				
10	0.0311	-0.0424	0.0637	-0.0563	0.0714	
20	0.0324	-0.0412	0.0648	-0.0552	0.0712	
30	0.0336	-0.0401	0.0659	-0.0541	0.0711	
50	0.0354	-0.0383	0.0681	-0.0521	0.0707	
70	0.0368	-0.0366	0.0707	-0.0504	0.0704	
80	0.0374	-0.0359	0.0715	-0.0497	0.0702	
90	0.0379	-0.0352	0.0727	-0.0489	0.0700	

puter work to understand the consequences when the integrations were prematurely terminated at some arbitrary values of r . The results of very extensive calculations showed that the good values of A_i and B_i were obtainable when the chosen upper limit in r was $r_{\max} \geq 10 \text{ \AA}$. As a matter of fact, beyond this value of $r_{\max}$, the RDF practically merged with the uniform distribution that might be observed if the atoms in the liquids were

treated like those in gases. The values of A_i and B_i evaluated in this way were used in the subsequent discussions. As an example, the effective values for one of the compositions, i.e., 10 per cent solute are given in Table 2.

(c) Interpretation of the theoretical results

The fractional changes, $\Delta S/S$ of the alloys were calculated for atomic concentration below 50 per cent of the solute. These results can now be compared with the experimental results reported earlier[34, 35, 38]. In particular, we show in Table 3 the initial slopes of the $\Delta S/S$ vs. concentration plots. This quantity Γ , as can be seen, are different for different solutes. That the present approach gives the right sign and right trend of $\Delta S/S$ in the above alloy systems needs some explanation. The shape and sign of the $\Delta S/S$ curve are strongly sensitive to the coefficients A_i and B_i . Of these two coefficients, B_i weights $\Delta S/S$ more heavily than A_i . For solvent In

Table 2. Effective values of the coefficients A_i and B_i for different solutes of the In-10% solute alloys

Solute	A_0	A_1	A_2	B_0	B_1	B_2
Hg	0.202	-0.899	2.715	-0.217	0.597	-0.428
Tl	0.193	-0.876	2.703	0.220	-0.609	0.456
Ga	0.234	-0.997	2.891	-0.225	0.618	-0.445
Pb	0.190	-0.870	2.700	0.221	0.612	0.463
Sn	0.196	-0.884	2.707	-0.219	0.605	-0.446
Pure In	0.197	-0.887	2.709	-0.219	0.603	-0.442

Table 3. Values of the initial slopes, $\Gamma = d[\Delta S/S]/dc$ of the $\Delta S/S$ versus concentration plots for the theoretical and experimental results

Solute	$\Gamma(\text{the})$	$\Gamma(\text{exp})$	$\Gamma(\text{the})/\Gamma(\text{exp})$
Hg	0.090	0.076	1.18
Tl	-0.128	-0.145	0.86
Ga	0.090	0.049 ^[a]	1.11
		0.030 ^[b]	
		0.081 ^[c]	
Pb	-0.134	-0.100	1.34
Sn	0.087	0.083	1.05

[a] From Ref. [38].

[b] From Ref. [35] using lower portion of the experimental curve.

[c] From Ref. [35] using upper portion of the experimental curve.

atom, we found that the even order A_l and odd order B_l are positive while the odd order A_l and even order B_l are negative (see Table 2 for one of the alloys). Now supposing $A_0 = m$, to a good approximation we may say for liquid In alloys

$$\Delta S/S = c_1 m [\sin^2 \eta_0 - \sin 2\eta_0 - 4\sin^2 \eta_1 + 3\sin 2\eta_1]. \quad (5.3)$$

Rigney and Flynn[9] argued that a negative change in $\Delta S/S$ is due to core scattering (i.e., d and f scattering, which means the terms involving η_2 and η_3). Then the above equation immediately tells us that in liquid In-Tl and In-Pb alloys one should expect $\eta_1 > \arctan \frac{1}{2}$ and $\eta_0 > \arctan 2$.

We suggest here an alternative interpretation. We believe that the positive and negative changes in $\Delta S/S$ are respectively caused by the attractive and repulsive scattering potentials of the ions in the alloy. An attractive potential gives positive values of η_l and a repulsive potential negative values of η_l . We suggest that in In-Tl and In-Pb alloys the scattering potentials are repulsive which make η_l negative. Whatever may be the nature of the potentials the contribution of the first term in equation (3.4) to $\Delta S/S$ remains unaffected; however, the sign of the second

term gets reversed when the behavior of the potential changes from one form to the other. Further, we believe that a transformation of this type takes place in liquid In-Hg alloys with increasing concentration of Hg, which perhaps produces the small hump as observed experimentally[38]. Here, the calculations for In-Hg alloys were done with the attractive potential only and, therefore, it is unlikely that the bending of the $\Delta S/S$ curve with concentration, as seen experimentally, can be seen even if the calculations are extended above 50 per cent of the solute.

The overall agreement between the theoretical and experimental results is reasonably good for the dilute In-alloys. It would be reasonable to anticipate that a better agreement could have been reached particularly in this region, had we used the solvent partial radial densities, which unfortunately cannot be at present obtained for most liquid alloys. An estimate was made for the solute rich alloys also, and a quantitative disagreement between the predicted and experimental data (above about 70 per cent solute) was observed. Several excuses may be made for this discrepancy at large solute concentration. Here we mention just two important ones. Firstly, the Odle-Flynn theory is inadequate for large δ_0 . Secondly and more importantly, it appears that the changes in the spin paramagnetic susceptibility which we have neglected may be far from being trivial. These two conditions are not met in the present theory.

6. CONCLUSIONS

In conclusion we emphasize that the presence of volume dilation and formation of atomic pairing in liquid alloys do affect the solvent Knight shift. This consideration enabled us to calculate the fractional change of the Knight shift using the partial wave phase shift data over larger composition range of the solute than previously been studied. The phase shifts can be obtained from differential scattering cross section of

the free electrons assuming that it is equivalent to the pseudopotential scattering cross section under the Born approximation.

With the above prescription an improved quantitative explanation of the fractional change of the Knight shift of the solvent In atom in dilute liquid In-Hg, In-Ga, In-Tl, In-Sn and In-Pb alloys, has been achieved. We can summarize here the three major sources that contributed to this remarkable improvement. The first one is the consideration of the effect of dilation that becomes rather important when the Fermi radius of the solvent changes quite significantly across the range of solute concentration. The second one is the careful handling of the coefficients A_l and B_l which are strongly sensitive to the nature of the solute, and also the functions of the radial distance. A treatment described in the text appears to be quite satisfactory and encouraging. The third one is the pseudopotential calculation of the phase shifts. When the Animalu-Heine pseudopotentials are used after proper corrections, the results are more reliable and useful.

REFERENCES

1. HANABUSA M. and BLOEMBERGEN N., *J. Phys. Chem. Solids* **27**, 363 (1966).
2. MOULSON D. J. and SEYMOUR E. R. W., *Adv. Phys.* **16**, 449 (1967).
3. WAGNER C. N. J. and HALDER N. C., *Adv. Phys.* **16**, 241 (1967).
4. HALDER N. C. and WAGNER C. N. J., *J. chem. Phys.* **47**, 4385 (1967).
5. FABER T. E. and ZIMAN J. M., *Phil. Mag.* **11**, 153 (1965).
6. ASHCROFT N. W. and LEKNER J., *Phys. Rev.* **145**, 83 (1966).
7. HALDER N. C. and WAGNER C. N. J., *Z. Naturf.* **23a**, 992 (1968).
8. ODLE R. L. and FLYNN C. P., *Phil. Mag.* **13**, 699 (1966).
9. RIGNEY D. A. and FLYNN C. P., *Phil. Mag.* **15**, 1213 (1967).
10. FLYNN C. P., RIGNEY D. A. and GARDNER J. A., *Phil. Mag.* **15**, 1255 (1967).
11. GARDNER J. A. and FLYNN C. P., *Phil. Mag.* **15**, 1233 (1967).
12. WATSON R. E., BENNETT L. H. and FREEMAN A. J., *Phys. Rev. Lett.* **20**, 653 (1968).
13. ZIMAN J. M., *Phil. Mag.* **6**, 1013 (1961).
14. PHILLIPS J. C. and KLEINMAN L., *Phys. Rev.* **116**, 287 (1959).
15. BLANDIN A. and DANIEL E., *J. Phys. Chem. Solids* **10**, 126 (1959).
16. WISER N., *Phys. Rev.* **143**, 339 (1966).
17. HEINE V. and WEAIRE D., *Phys. Rev.* **152**, 603 (1966).
18. SCHNEIDER T. and STOLL E., *Adv. Phys.* **16**, 731 (1967).
19. FABER T. E., *Adv. Phys.* **15**, 547 (1966).
20. HALDER N. C., *Phys. Rev.* **177**, 471 (1969).
21. HALDER N. C., *J. chem. Phys.* **52**, 5450 (1970).
22. DANIEL E., *J. Phys. Radium* **20**, 769 (1959); **20**, 849 (1959).
23. BLATT F. J., *Phys. Rev.* **108**, 285 (1957).
24. FRIEDEL J., *Adv. Phys.* **3**, 446 (1954).
25. KOHN W. H. and VOSKO S. H., *Phys. Rev.* **119**, 912 (1960).
26. MEYER A., NESTOR C. W. and YOUNG W. H., *Proc. Phys. Soc. (London)* **92**, 446 (1967).
27. THORNTON D. E. and YOUNG W. H., *J. Phys. C. (Proc. Phys. Soc.)* **1**, 1097 (1968).
28. ANIMALU A. O. E. and HEINE V., *Phil. Mag.* **12**, 1249 (1965).
29. FABER T. E., *Adv. Phys.* **16**, 637 (1967).
30. MORSE P. M. and FESHBACH H., *Methods of Theoretical Physics*, Vol. II, p. 1066. McGraw Hill, New York (1953).
31. HARRISON W. A., *Pseudopotentials in the Theory of Metals*, p. 19. W. A. Benjamin, New York (1966).
32. GREEN M. D. and KOHN W., *Phys. Rev.* **137A**, 513 (1965).
33. ASHCROFT N. W., *Phys. Lett.* **23**, 48 (1966).
34. SEYMOUR E. F. W. and STYLES G. A., *Proc. Phys. Soc.* **87**, 473 (1966).
35. VAN DER LUGT W. and VAN DER MOLEN S. B., *Phys. Status Solidi* **19**, 327 (1967).
36. OCKEN H. and WAGNER C. N. J., *Phys. Rev.* **49**, 122 (1966).
37. STOCKS G. M., YOUNG W. H. and MEYER A., (Private communication).
38. MOULSON D. J. and SEYMOUR E. F. W., *Adv. Phys.* **16**, 449 (1967).

VAPOR-CRYSTAL EQUILIBRIUM AND ELECTRICAL PROPERTIES OF HgTe*

A. J. STRAUSS and R. F. BREBRICK

Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, Mass. 02173, U.S.A.

(Received 2 December 1969; in revised form 28 January 1970)

Abstract—The vapor-crystal equilibrium of HgTe has been investigated by measuring the electrical properties of samples which were quenched after having been annealed at 150–550°C long enough to reach equilibrium with either (1) a liquid Hg reservoir, (2) a two-phase Hg-rich or Te-rich ingot, or (3) internal Te-rich microprecipitates. Except in a few cases, the electrical measurements showed conclusively that the samples were *p*-type. Hall coefficient measurements at 4.2°K and about 100 kG could be used to determine the value of $(p - n)$ for samples with $(p - n)$ exceeding $4 \times 10^{16} \text{cm}^{-3}$. Less *p*-type samples could be arranged in order of $(p - n)$ by comparing their values of the Seebeck coefficient at 300°K and the low-field Hall coefficients at 300 and 77°K. For samples annealed at 550°C, $(p - n)$ increases monotonically with decreasing Hg pressure from $4.7 \times 10^{16} \text{cm}^{-3}$ for Hg saturation to about $9 \times 10^{16} \text{cm}^{-3}$ for Te saturation. Independent of any microscopic model, this variation shows that $(p - n)$ increases monotonically with increasing Te content. According to the simplest microscopic model, the predominant point defects are Hg-vacancy or Te-interstitial acceptors, and above 450°C the entire homogeneity range lies on the Te-rich side of the stoichiometric composition. Along both the Te-rich and Hg-rich solidus lines the Te content increases with increasing temperature. The value of $(p - n)$ extrapolated to the maximum melting point is about $1.5 \times 10^{16} \text{cm}^{-3}$.

1. INTRODUCTION

THE ELECTRICAL and optical properties of the II–VI compound HgTe and its solid solutions with CdTe have been the subject of numerous investigations[1]. These studies have shown that HgTe is a semi-metal whose band structure is quite similar to that of gray tin. They have also shown that HgTe grown from an undoped stoichiometric melt is strongly *p*-type, and that the net hole concentration, $(p - n)$, can be reduced by annealing in sufficiently high pressures of Hg vapor. It is generally believed that the excess holes result from the ionization of acceptor defects associated with the presence of a stoichiometric excess of Te. In physico-chemical studies, the partial pressures of Hg(g) and Te₂(g) in equilibrium with Hg-saturated and Te-saturated HgTe have been measured as a function of temperature[2], the liquidus lines of the Hg–Te system have been determined

[1, 2], and the electrical properties have been investigated as a function of the temperature and Hg partial pressure[3, 4].

In the present investigation, the vapor-crystal equilibrium of HgTe has been studied by means of annealing experiments in which undoped HgTe samples were either equilibrated with a vapor phase containing Hg(g) and Te₂(g) at partial pressures determined by the temperature and composition of an external condensed phase or equilibrated with an internal phase probably consisting of Te-rich microprecipitates. The annealed samples were then characterized by measurements of Hall coefficient, resistivity, and Seebeck coefficient. Except in a few cases, the results of these measurements showed conclusively that the samples were *p*-type. (In this paper, a sample is designated as *p*-type if it contains more holes than electrons, even though its Hall and Seebeck coefficients may be negative because of the high ratio of electron to hole mobility in HgTe). For samples with net hole concentrations

*This work was sponsored by the Department of the Air Force.

exceeding $4 \times 10^{18} \text{cm}^{-3}$, the values of $(p-n)$ were found by Hall coefficient measurements at 4.2°K and 100–110 kG. For samples with lower net hole concentrations, $(p-n)$ could not be evaluated in this way, since these samples contained too many conduction electrons at 4.2°K for a simple Hall equation to be applicable even at 110 kG, the highest magnetic field available. However, it was possible to arrange these samples in order of decreasing $(p-n)$ by means of comparisons among their electrical properties.

The experimental methods mentioned have been used to obtain $(p-n)$ as a function of $\text{Hg}(g)$ pressure for samples annealed at 550°C, as a function of temperature between 150–550°C for Te-saturated samples, and as a function of temperature between 450–550°C for Hg-saturated samples. The implications of the experimental results for the stoichiometry of HgTe will be discussed first without assuming any microscopic model for the lattice defects and then in terms of the simplest acceptor defect model.

In an earlier study Rodot[3] gave values of $(n-p)$, assumed equal to $-1/eR_{77}$, for the Hg-rich portion of the HgTe homogeneity range and for temperatures below 400°C and also proposed a defect model for HgTe.

2. EXPERIMENTAL

Electrical measurements

The HgTe samples were large-grained rectangular parallelepipeds with dimensions of about $2 \times 4 \times 15$ mm. They were cut from ingots grown by the Bridgman method from undoped melts prepared by direct reaction of the semiconductor-grade elements. Electrical measurements were made on each sample before and after it had been treated by one of the annealing methods described below. The Seebeck coefficient relative to iron was measured at an average sample temperature of about 28°C by means of a pressure-contact apparatus which produced a temperature difference of about 6°C between the ends of the sample. The relative value was converted

to the absolute Seebeck coefficient by algebraic addition of $+11 \mu\text{V}/^\circ\text{K}$, the absolute value for iron. The Hall coefficient at about 6 kG and the resistivity at zero field were measured with pressure contacts at room temperature and at 77°K. For selected samples, the Hall coefficient at 4.2°K was measured with soldered indium contacts as a function of magnetic field up to 100–110 kG. All the electrical measurements were made by conventional d.c. potentiometric techniques.

Equilibration with liquid Hg reservoir

In one type of annealing experiment, HgTe samples were annealed at 550°C in a closed tube containing liquid Hg heated to a lower temperature. The Hg temperature was adjusted to establish a partial pressure of Hg intermediate between the limiting pressures [2] characteristic of Hg- and Te-saturated HgTe at 550°C. Equilibration with such vapors produced HgTe samples with compositions lying inside the homogeneity range of HgTe at 550°C.

In each experiment, 2 HgTe samples with different initial compositions were placed at one end of a 12 mm o.d. silica tube 64 cm long, which had been cleaned with HF and distilled water. Pure liquid Hg (between 0.2–2 g, depending on the partial pressure desired) was placed at the other end of the tube, which was then evacuated with a mechanical pump and sealed. The tube was placed at the center of a horizontal annealing furnace formed by butting together 2 separate resistance furnaces each 61 cm long. During the annealing run, the end of the tube containing the HgTe samples was heated to $550 \pm 4^\circ\text{C}$. The other end was made the coldest part of the tube, and therefore a reservoir of liquid mercury remained there through the run. The reservoir temperature was kept constant to $\pm 3^\circ\text{C}$. After annealing for 168 hr, the end of the tube containing the HgTe samples was pulled out of the furnace and rapidly cooled to room temperature by pouring water over it. The

entire tube was then cooled to room temperature, and the samples were removed for electrical measurements.

At 550°C, the ratio of $\text{Hg}(g)$ partial pressure to $\text{Te}_2(g)$ partial pressure is about 1000:1 for Te-saturated HgTe , and even larger for other compositions [2]. Therefore it was assumed that the liquid Hg reservoir was not contaminated by Te during the run, and that the partial pressure of $\text{Hg}(g)$ in equilibrium with the HgTe samples was equal to the saturation vapor pressure of liquid Hg at the reservoir temperature. Reservoir temperatures between 345–509°C were employed, corresponding to $\text{Hg}(g)$ partial pressures between 0.80–9.0 atm. The $\text{Hg}(g)$ partial pressures over Te- and Hg-saturated HgTe at 550°C are 0.52 and 11 atm, respectively [2].

Isothermal equilibration with two-phase ingots

In a second type of annealing experiment, HgTe samples were equilibrated isothermally through the vapor phase with an ingot whose composition was outside the homogeneity range of $\text{HgTe}(c)$ and inside the liquidus line at the annealing temperature. The ingot therefore consisted of $\text{HgTe}(c)$ at one homogeneity limit and a liquid phase. By the Gibbs phase rule, fixing the temperature determines all of the intensive properties of the system, including the $\text{Hg}(g)$ and $\text{Te}_2(g)$ partial pressures. Samples annealed with such ingots become as Hg-rich or as Te-rich as possible at the annealing temperature, depending on whether the ingot contains excess Hg or excess Te, respectively. The principle of the method and its application to PbTe have been described previously [5].

The HgTe samples were annealed in an evacuated silica tube, 3 in. long, which contained a silica shelf to separate them from the ingot. The tube was first cleaned with HF, rinsed with distilled water, and outgassed for 16 hr at 1020°C and 3×10^{-7} torr. Four samples were placed on one side of the shelf, and a mixture of unreacted Hg and Te

weighing 15 g was placed on the other side. The composition of the mixture was 45 at. % Te for Hg-saturation and 55 at. % Te for Te-saturation. The loaded tube was sealed on a vacuum system maintained at 10^{-5} to 10^{-6} torr, pumped at room temperature for 1 hr, and sealed off. The preferential loss of Hg during pumping was not sufficient to cause a significant change in ingot composition.

The tube was placed in a resistance-heated muffle furnace and heated to the annealing temperature, which was 445 or 550°C for Hg-saturation and 550°C for Te-saturation. At these temperatures, the elements are known [2] to react rapidly to establish the $\text{Hg}(g)$ and $\text{Te}_2(g)$ partial pressures characteristic of saturated HgTe . The annealing time was 160 or 320 hr at 450°C and 160 hr at 550°C. At the end of this time, the tube was removed from the furnace and immediately immersed in water, after which the quenched samples were removed from the tube for electrical measurements.

For each experiment of this type, the average composition of the condensed phases (HgTe samples plus two-phase ingot) at the annealing temperature was calculated from the total weight of the samples, the weights of Hg and Te used, the volume of the silica tube, and the partial pressures of $\text{Hg}(g)$ and $\text{Te}_2(g)$ in equilibrium with Hg- or Te-saturated HgTe [2]. In each case the calculated composition was within 1 at. % of either 45 or 55 at. % Te, and therefore was well outside the homogeneity range of HgTe , as required for the preparation of saturated samples. Analysis of vapor pressure data [2] has shown that the minimum Te content of HgTe is at least 49.9 at. % Te, and that the maximum Te content does not exceed 50.6 at. % Te.

Equilibration with an internal Te-rich microprecipitate

In the remaining experiments, HgTe samples were equilibrated with a precipitated internal phase instead of an external vapor phase. These experiments were undertaken

on the basis of measurements on HgTe samples saturated with Te at 550°C, which showed that the net hole concentration decreased with a decrease in the rate of cooling from 550°C to room temperature. This result indicated that below 550°C there is a range of temperatures within which (1) the solubility of Te in HgTe decreases with decreasing temperature, and (2) Te present in excess of the solubility limit is rapidly removed from the HgTe lattice by local precipitation to form a dispersed second phase of Te-rich microprecipitates. In this temperature range, therefore, Te-saturated HgTe can be obtained at a temperature T below 550°C by first Te-saturating at 550°C with a two-phase ingot, annealing at T to establish equilibrium with the precipitated phase, and then quenching. Such a procedure has been used to investigate the solubility of Te in PbTe[6, 7] and Pb in PbS[8].

In most of the precipitation experiments, a sample of HgTe Te-saturated at 550°C was placed in a 12 mm o.d. silica tube 7.5 cm long, which had been cleaned with HF and distilled water. (A few experiments were performed on samples initially saturated with Hg at 550°C.) The tube was flushed several times with helium gas, filled with 0.5 atm of helium, and sealed. The tube was then suspended by a wire at the center of a vertical resistance furnace and heated to an annealing temperature between 150–550°C. At the end of the run, the sample was quenched to room temperature by cutting the support wire, which allowed the tube to drop into a beaker containing 2.5 l of a solution of 10 wt. % NaCl in water. The sample was then removed for electrical measurements. In order to be sure of attaining equilibrium, this process was repeated for successively longer annealing times until there was no further change in the electrical properties of the sample.

3. RESULTS

Electrical properties

The Hall coefficient at 4.2°K, $R_{4.2}$, was

measured as a function of magnetic field between 5–6 and 100–110 kG for 20 annealed samples of HgTe, all of which were found to be p -type. Table 1 presents data on the electrical properties of 10 representative samples, which were either Te-saturated or Hg-saturated. Within each group the samples are listed in order of decreasing net hole concentration, $(p-n)$. For 5 of these samples, indicated by an asterisk on the value of $R_{4.2}$ (100 kG), the value of the Hall coefficient at 4.2°K was almost independent of magnetic field. This behavior shows there was no appreciable electron contribution to the conductivity, even at low fields. The corresponding value of $(p-n)$ was therefore calculated from the expression $(p-n) = 1/eR_{4.2}$ (100 kG). For these samples, $(p-n)$ is seen to be between $4.5\text{--}8.1 \times 10^{18} \text{ cm}^{-3}$.

For the other 5 samples listed, $R_{4.2}$ is negative at 5 kG and decreases markedly in absolute value with increasing field, even becoming positive in two cases. Similar observations on HgTe have been reported by Stradling and Antcliffe[9] and by Harman *et al.*[10]. As these authors have shown by detailed theoretical analysis, the strong field dependence of $R_{4.2}$ is characteristic of p -type samples in which electrons make an appreciable contribution to the conductivity at low magnetic fields. Even in samples with $(p-n)$ exceeding 10^{18} cm^{-3} , such a contribution is possible at 4.2°K because (1) HgTe is a semi-metal and therefore has a high intrinsic carrier concentration even at very low temperatures, and (2) HgTe has a very high ratio of electron to hole mobility, of the order of 100.

Values of $(p-n)$ have not been obtained directly for the 5 samples just described. It had been hoped that the limiting expression $(p-n) = 1/eR_H$ would become applicable at the highest magnetic fields available, where the mobility-field product μB is much greater than one for electrons and much less than one for holes. This was not the case, however, since $R_{4.2}$ did not reach a constant value even

Table 1. Electrical properties of Te-saturated and Hg-saturated HgTe

Anneal temp. (°C)	Anneal durations (hr)	α 300°K	at 6 kG 77°K				4.2°K		4.2°K, 100 kG $R_{4,2}$	$(p-n) \times 10^{-18}$
			R_{300}	$R_{300}\sigma$	R_{77}	$R_{77}\sigma$	$R_{4,2}$	$R_{4,2}\sigma$		
Te-saturated HgTe										
495	1	+37.0	-9.03	1.87(10 ³)	+0.735	132	+0.788	132	+0.791*	131
450	6, 10	+7.8	-14.1	2.93(10 ³)	+0.860	131	+0.943	111	+0.925*	105
400	16, 40	-43.1	-18.9	4.61(10 ³)	+0.951	126	+1.17	131	+1.17*	127
348	25	-127	-25.5	7.99(10 ³)	+0.303	29.7	+1.66	119	+1.50*	102
290	4, 24	-145	-20.6	1.58(10 ⁴)	-18.0	1.59(10 ³)	-0.828	28.4	-1.74	-
250	48, 96	-137	-18.5	1.88(10 ⁴)	-68.0	3.81(10 ³)	-4.97	195	-1.65	(3.53)
200	24, 72	-125	-17.5	2.40(10 ⁴)	-109	1.71(10 ⁴)	-93.0	1.62(10 ³)	+0.949	(2.82)
150	336, 772	-119	-16.1	2.17(10 ⁴)	-79.0	2.08(10 ⁴)	-123	2.70(10 ³)	-20.6	(2.02)
Hg-saturated HgTe										
550	160	-128	-23.0	7.99(10 ³)	-6.26	509	+0.95	-	+1.34*	83.8
445	288	-128	-15.8	2.2(10 ⁴)	-95.0	1.9(10 ⁴)	-311	2.82(10 ⁴)	+4.30	-

α is the absolute Seebeck coefficient in $\mu V/^\circ K$. R is the Hall coefficient in $cm^3 C^{-1}$, and $R\sigma$ is the Hall mobility in $cm^2 V^{-1} sec^{-1}$. When the Hall constant at 4.2°K had saturated by 100 kG an asterisk is attached to the corresponding value. The values of $(p-n)$ given in the last column, except for those in parentheses, were calculated from the saturation value of $R_{4,2}$ as described in the text. The values in parentheses were estimated as described in Results, Net Hole Concentration of Te-Saturated HgTe.

at 110 kG. Although methods have been described for obtaining p and n by analyzing the field dependence of R_H , the data obtained for the 5 samples are not sufficiently detailed to permit such an analysis. (For these samples, the values of $R_{4.2}$ at 110 kG appear to be inconsistent. The sign of this quantity is negative for the samples Te-saturated at 290, 250, and 150°C and positive for the sample Hg-saturated at 445°C, although on the basis of $R_{4.2}$ at 6 kG and the electrical properties at higher temperatures the former three samples have higher values of $(p-n)$ than the latter. Positive values of $R_{4.2}$ at high fields were also reported by Stradling and Antcliffe[9] and by Harman *et al.*[10] for samples with lower values of $(p-n)$. These apparent inconsistencies are not very surprising, since the magnetic field dependence of $R_{4.2}$ and the magnitude of the field required for saturation are expected to be much more sensitive than the properties at higher temperatures to differences in the ratio of electron to hole mobility.)

Figure 1 shows the Hall coefficients at 6 kG and 300°, 77° and 4.2°K and Fig. 2 shows the absolute Seebeck coefficient at 300°K (α_{300}), all as functions of $(p-n)$. The solid points represent samples, including those in Table 1, for which $(p-n)$ could be calculated from the high field value of $R_{4.2}$. For the open points the values of $(p-n)$ were obtained by extrapolation of the Te-rich solidus curve, as discussed below. The two figures show that the low field Hall and Seebeck coefficients may be negative even for strongly p -type HgTe, as a result of the high intrinsic carrier concentration and mobility ratio. Thus α_{300} is positive only for $(p-n)$ values exceeding $7 \times 10^{18} \text{ cm}^{-3}$, R_{300} is negative over the entire range investigated, and R_{77} is positive only for $(p-n)$ values exceeding $4 \times 10^{18} \text{ cm}^{-3}$. For $(p-n)$ greater than $5.5 \times 10^{18} \text{ cm}^{-3}$, R_{77} and $R_{4.2}$ have almost the same value.

The correlations among the electrical properties of HgTe at 77° and 300°K are shown in a different way in Figs. 3-5, which

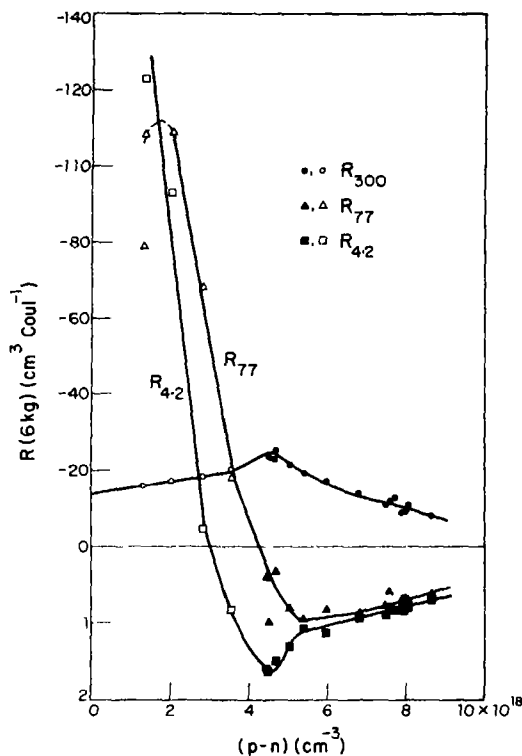


Fig. 1 Hall coefficients at 6 kG and 300, 77, and 4.2°K plotted against net hole concentration, $(p-n)$. For the solid points, $(p-n) = 1/eR$, where R is the value of the Hall coefficient at 4.2°K and ~ 100 kG. For the open points, $(p-n)$ was obtained by assuming that $(p-n)$ for Te-saturated HgTe at temperatures below 350°C is given by extrapolation of the upper straight line in Fig. 7. Note the expanded ordinate scale for positive values of the Hall coefficient.

respectively are plots of α_{300} vs. R_{300} , α_{300} vs. R_{77} , and the Hall mobility, $R\sigma$, at 77°K vs. R_{77} . These figures include data for all the samples and not just those for which $(p-n)$ has been determined. For completeness, data are also included for n -type samples (indicated by triangles) prepared in an earlier investigation by doping with In and Hg-saturating at 350°C[11]. The squares labeled with values of $(p-n)$ in Figs. 3-5 were obtained from the plots of Figs. 1 and 2. These squares of course are distributed only along the strongly p -type portion of each curve. The value of $(p-n)$

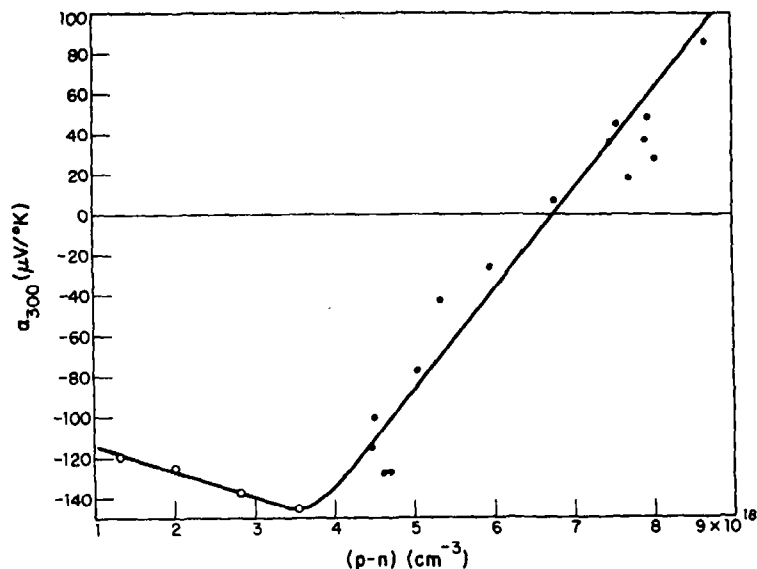


Fig. 2. Absolute Seebeck coefficient at 300°K (α_{300}) as a function of $(p-n)$. The solid and open points have the same significance as in Fig. 1.

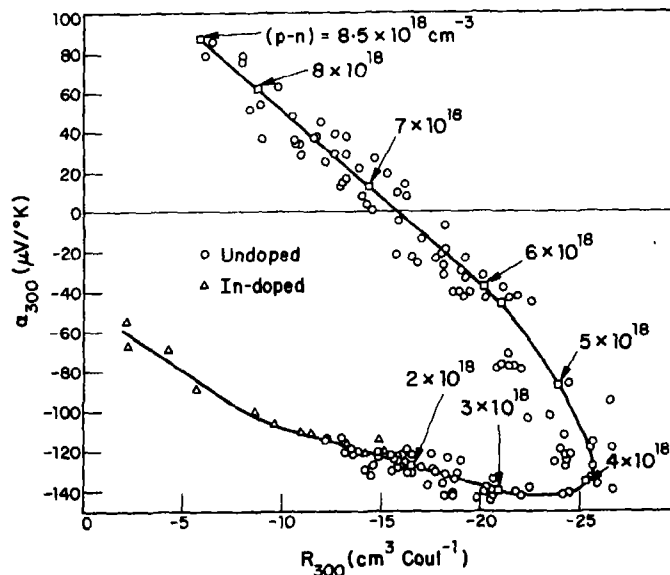


Fig. 3. Absolute Seebeck coefficient at 300°K (α_{300}) as a function of Hall coefficient at 6 kG and 300°K (R_{300}). The triangles represent In-doped HgTe that has been Hg-saturated. The circles are for undoped HgTe annealed at various temperatures and Hg pressures. The squares labeled with values of $(p-n)$ were obtained from the smoothed curve in Fig. 2. For intrinsic HgTe, $\alpha_{300} \approx -120 \mu\text{V}/^\circ\text{K}$ and $R_{300} \approx -15 \text{ cm}^3 \text{ C}^{-1}$.

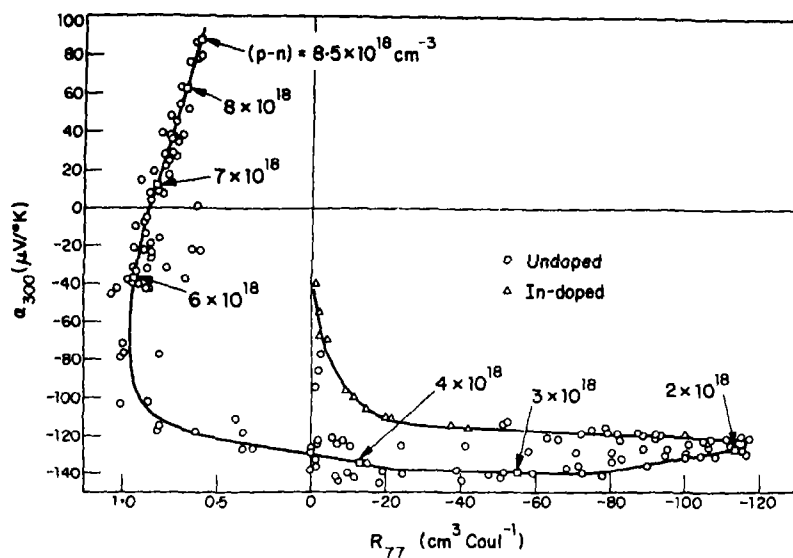


Fig. 4. Absolute Seebeck coefficient at 300°K (α_{300}) as a function of Hall coefficient at 6 kG and 77°K (R_{77}). The abscissa scale for positive values of R_{77} is greatly expanded relative to that for negative values. The symbols have the same significance as in Fig. 3.

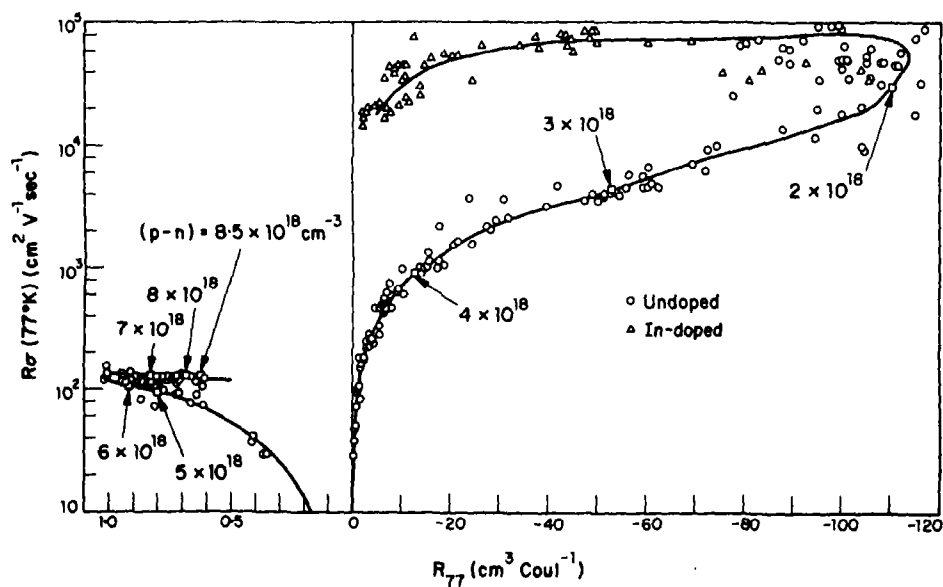


Fig. 5. The Hall mobility ($R\sigma$) as a function of the Hall coefficient (R_{77}), both at 77°K and 6 kG. The symbols have the same significance as in Figs. 3 and 4.

continues to decrease monotonically along the entire curve in the direction away from the squares. Thus by employing Figs. 3-5, electrical measurements at 77 and 300°K can be used to obtain approximate values of $(p-n)$ for samples with $(p-n)$ above $1.3 \times 10^{18} \text{ cm}^{-3}$, and in every case to arrange samples in order of decreasing $(p-n)$.

Figures 3 and 4 show that the most negative value for α_{300} is $-145 \mu\text{V}/^\circ\text{K}$. For the most strongly p -type samples, Fig. 5 shows that $R\sigma$ is equal to the hole mobility, which is $120 \pm 10 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$ in most cases. Along the upper leg of the curve, where $R\sigma$ ranges from about 1.5×10^4 to a maximum of $9 \times 10^4 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$, it is equal to the electron mobility. In the intermediate, mixed conduction region, $R\sigma$ is not simply related to either the electron or hole mobility.

Scattered values for the electrical properties of HgTe have been reported by a number of authors. Our results are generally in good agreement with theirs. For example, Giriat[12] has measured various properties of as-grown HgTe and HgTe annealed in Hg vapor at 250 and 300°C. The most negative value he observed for α_{300} was $-150 \mu\text{V}/^\circ\text{K}$. For a particular sample he found $R_{300}(6.2 \text{ kg}) = -17.5 \text{ cm}^3 \text{ C}^{-1}$, $R_{77}(6.2 \text{ kg}) = -104 \text{ cm}^3 \text{ C}^{-1}$, and $\alpha_{300} = -140 \mu\text{V}/^\circ\text{K}$. In good agreement we find (Figs. 3, 4) for $R_{300} = -17.5 \text{ cm}^3 \text{ C}^{-1}$ that $R_{77} = -104 \text{ cm}^3 \text{ C}^{-1}$ and $\alpha_{300} = -130 \pm 8 \mu\text{V}/^\circ\text{K}$.

Net hole concentration at 550°C as a function of Hg pressure

Figure 6 shows the net hole concentration, $(p-n)$, as a function of Hg pressure for samples annealed 160 hr at 550°C. The value of $(p-n)$ was obtained from the high field value of $R_{4.2}$ as described earlier. The range of Hg pressures over which HgTe is a stable phase at 550°C is indicated[2]. Inside this range the samples were equilibrated at fixed Hg pressures determined by the temperature of a Hg reservoir. The attainment of equilibrium was established by the observation that

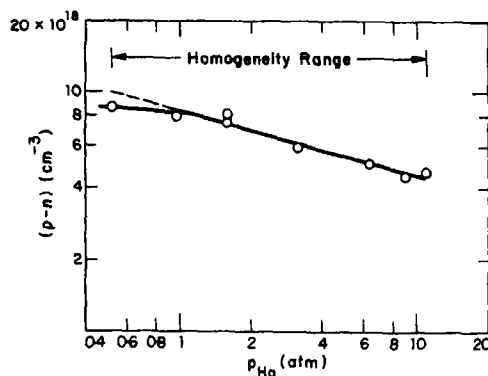


Fig. 6. The value of $(p-n)$ for HgTe annealed at 550°C as a function of the Hg-pressure during annealing (p_{Hg}).

pairs of crystals annealed together had the same electrical properties although initially one had a higher $(p-n)$ and the other a lower $(p-n)$ than the final value. The sample at the Hg-rich homogeneity limit was isothermally equilibrated with a two-phase ingot. The sample at the Te-rich limit was first equilibrated with a 55 at. % Te ingot in an evacuated shelf-tube, quenched, re-annealed for 5 min in a tube filled with helium (as in the internal precipitation experiments), and quenched. After the first quench, $(p-n)$ was $7.8 \times 10^{18} \text{ cm}^{-3}$, significantly lower than the value of $8.7 \times 10^{18} \text{ cm}^{-3}$ obtained after the second quench and even below that obtained by equilibration under a Hg pressure of 0.95 atm. The interpretation of these results is that the high temperature, Te-rich compositions of the HgTe phase are more nearly frozen-in by a quench using an He-filled silica tube than by a quench using an evacuated shelf tube.

It is seen in Fig. 6 that $(p-n)$ is positive and decreases monotonically with increasing Hg pressure over the entire homogeneity range. The points cannot be represented by a single straight line with the precision we feel is warranted by that of the measurements. In view of the quench rate effects encountered, it is possible that the highest value of $(p-n)$ is still too low due to an insufficiently rapid quench. The line shown at higher Hg pressures has a slope of -0.27 .

Net hole concentration of Te-saturated HgTe

The values of $(p-n)$ for Te-saturated HgTe at various temperatures are shown along the upper line of Fig. 7. The point at 550° was also plotted in Fig. 6. (Any reasonable straight line drawn in Fig. 7 through the 4 points for Te saturation at temperatures below 550°C gives a value of $(p-n)$ for Te-saturation at 550°C that is below $9.5 \times 10^{18} \text{ cm}^{-3}$. This is not high enough to completely eliminate the curvature of the isotherm shown in Fig. 6 and suggests this curvature is not entirely due to quench effects.) The points below 550°C were obtained for samples equilibrated with an internal, Te-rich microprecipitate. These samples were initially Te-saturated at 550°C by isothermal equilibration with a two-phase ingot. They were then annealed at various low temperatures and quenched. The annealing temperatures and times are given in the first and second columns of the first section of

Table 1. Where two annealing times are given in the same row, the same electrical properties were reached after each anneal. We assume this steady state represents equilibrium.

The points for Te-saturated samples in Fig. 7 are fit well by a straight line, $(p-n) = 6.32 \times 10^{19} \exp [s/kT]$ with $s = -0.141 \text{ eV}$. No $(p-n)$ values could be obtained for samples equilibrated below 350°C, since these samples were not sufficiently p -type for $R_{4,2}$ to be independent of magnetic field. However, comparison of their electrical properties (see Table 1) with the data of Figs. 3-5 shows that $(p-n)$ continues to decrease monotonically with decreasing temperature down to 150°C, the lowest annealing temperature used.

To obtain estimated $(p-n)$ values for the samples which were Te-saturated below 350°C, we have extrapolated the straight line of Fig. 7 representing Te-saturation down to

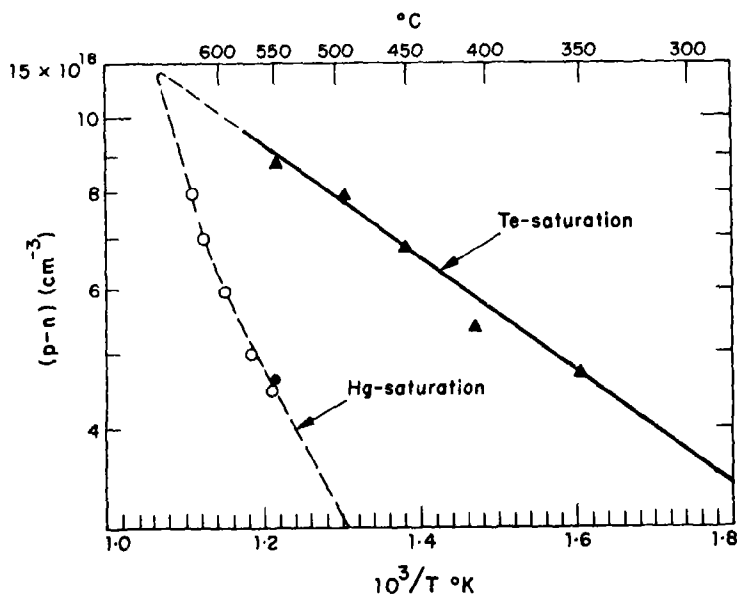


Fig. 7 The value of $(p-n)$ for Te-saturated HgTe (upper line) and for Hg-saturated HgTe (lower line) as a function of the temperature of saturation. For the solid points the value of $(p-n) = 1/eR$, where R is the value of the Hall coefficient at 4.2°K and $\sim 100 \text{ kG}$. For the open points the value of $(p-n)$ was obtained by using Fig. 8, as explained in the text.

150°C. These estimated values, which are listed in parentheses in the last column of Table 1, have been used to obtain the open points shown in Figs. 1 and 2, thus extending the correlation between electrical properties and $(p-n)$ from $4.5 \times 10^{18} \text{ cm}^{-3}$ to $1.3 \times 10^{18} \text{ cm}^{-3}$. Within this range, we have found the values of $(p-n)$ obtained from the various electrical properties of a particular sample using Figs. 1 and 2 may differ by as much as a factor of 2. (The Te-saturation line is expected to show a discontinuity in slope at the eutectic temperature of 413°C. In making the straight line extrapolation described above, and in Fig. 7 itself, we have taken this change to be negligible. This assumption proves to be consistent with the results of the next section.)

Net hole concentration of Hg-saturated HgTe

Values of $(p-n)$ for Hg-saturated HgTe are shown along the lower, dashed line of Fig. 7. The value at 550°C (solid circle) was obtained from the high field value of $R_{4,2}$ and is also plotted in Fig. 6. Values of $(p-n)$ for samples Hg-saturated at 445°C could not be found in this manner. However these samples are p -type with values of $(p-n)$ lower than that for Hg-saturation at 550°C. Comparison of their electrical properties (Table 1) with Figs. 1 and 2 gives $(p-n) = (2.2 \pm 0.2) \times 10^{18} \text{ cm}^{-3}$. This value is dependent on the extrapolation of the Te-saturation line in Fig. 7 that enabled the range of $(p-n)$ in Figs. 1 and 2 to be extended below $4 \times 10^{18} \text{ cm}^{-3}$. It is therefore significant that it agrees with the extrapolation to 445°C of the straight line for Hg-saturation in Fig. 7. The open circles in Fig. 7 were obtained by extrapolation of the isoconcentration lines shown in Fig. 8 as explained in the Discussion. The uppermost portions of the Hg-saturation and Te-saturation lines are shown schematically in Fig. 7 by the dotted lines, which have been drawn to meet at the congruent melting point of HgTe, 670°C. It is seen that $(p-n)$ is in the neighborhood of $1.5 \times 10^{19} \text{ cm}^{-3}$ at the maximum melting point.

4. DISCUSSION

Net hole concentration as a measure of composition

The isotherm in Fig. 6 shows that $(p-n)$ increases monotonically with decreasing Hg pressure over the entire homogeneity range at 550°C. Rodot's results [3] in a lower range of $(p-n)$ and for several temperatures between 200–450°C are consistent with such a monotonic variation. From the thermodynamic criterion for a stable phase, the atom-fraction of Te, x_{Te} , must also increase monotonically with decreasing Hg pressure. Therefore we may conclude that $(p-n)$ increases monotonically with increasing x_{Te} , and the former thus gives a unique measure of the latter even though the precise functional relationship has not been experimentally established in a direct way. The lines in Fig. 7 can then be considered as the solidus lines for HgTe, although neither the origin or scale of the x_{Te} axis is fixed. To establish these requires a microscopic model. Such a model will be proposed in a later section.

Comparison of the solidus lines in Fig. 7 shows that the Hg-saturated solidus at 550° and the Te-saturated solidus at about 350°C have the same value of $(p-n)$ and therefore of x_{Te} . Thus a sample of HgTe that is Hg-saturated at 550°C will become Te-saturated upon cooling to 350°C. If this sample is annealed at some temperature below 350°C, it will approach an equilibrium condition of Te-saturation by the formation of internal, Te-rich microprecipitates in the same manner as samples initially Te-saturated above the annealing temperature. This has been directly demonstrated by an experiment in which a crystal was Hg-saturated at 550°C, annealed for 4 hr at 295°C in an ampoule containing Hg vapor at $\frac{1}{2}$ atm, and quenched in the usual manner for internal precipitation experiments. After the surface had been ground off, as expected the electrical properties of the samples were essentially the same as those of Te-saturated HgTe annealed at 295°C. (it should be noted that attainment of Te-satura-

tion could not have resulted from loss of Hg to the vapor phase. This was prevented because the Hg pressure during annealing at 295°C exceeded that required for Hg saturation. In fact the entire crystal would have become Hg saturated after a sufficiently long period. For the annealing time used, the approach to Hg saturation was restricted to a thin surface layer. However, this time was sufficient for equilibrium at the Te-rich solidus to be attained in the interior of the crystal by internal precipitation.)

P-T diagram for HgTe

The pressure-temperature diagram for HgTe is shown in Fig. 8. The highest and lowest curves give the Hg partial pressure (p_{Hg}) in equilibrium with Hg-saturated and Te-saturated HgTe, respectively. These

curves, which were determined earlier by optical absorption measurements[2], meet at the congruent melting point to form a three-phase loop enclosing those values of p_{Hg} and $10^3/T$ for which HgTe is a stable phase. The solid lines within this loop give p_{Hg} and $10^3/T$ for fixed values of $(p-n)$ between 4.5×10^{18} and $8.0 \times 10^{18} \text{ cm}^{-3}$. Each of these isoconcentration lines is determined by two points. The upper point gives the value of p_{Hg} , obtained from the smoothed isotherm (solid line) of Fig. 6, for which HgTe has the specified value of $(p-n)$ at 550°C. The lower point lies on the pressure curve for Te-saturated HgTe and gives the temperature, obtained from the upper line in Fig. 7, at which Te-saturated HgTe has this value of $(p-n)$.

(The temperature at which Hg-saturated

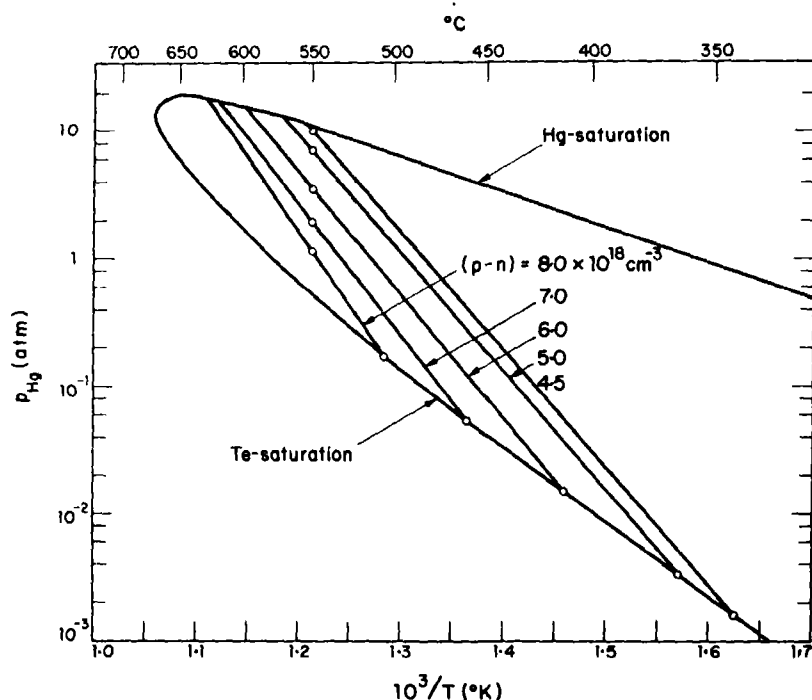


Fig. 8. P-T diagram for HgTe. The three-phase loop is shown as the outer, parabola-like curve on a plot of Hg pressure (p_{Hg}) vs. reciprocal absolute temperature. Each of the straight lines within this loop gives the $p_{\text{Hg}} - 10^3/T$ relationship for the labeled value of $(p-n)$.

HgTe attains a particular value of $(p-n)$ has been determined for temperatures above 550°C by making a short extrapolation of the isoconcentration lines in Fig. 8 and noting the temperature at which they intersect the Hg-rich three-phase line. These approximate results are shown as the open circles in Fig. 7.)

Since a fixed value of $(p-n)$ implies a fixed value of x_{Te} , the isoconcentration lines of Fig. 8 determine the partial gram-atomic enthalpy and entropy of Hg in HgTe measured relative to the corresponding quantities for Hg gas at 1 atm. The values are $\bar{h}_{\text{Hg}} = -43 \pm 1$ kcal/g-atom and $\bar{s}_{\text{Hg}} = -56 \pm 1$ e.u./g-atom for $(p-n)$ between 4.5 and $6 \times 10^{18} \text{ cm}^{-3}$. They become more negative with increasing $(p-n)$, and are $\bar{h}_{\text{Te}} = -54$ kcal/g-atom and $\bar{s}_{\text{Hg}} = -66$ e.u./g-atom at $8 \times 10^{18} \text{ cm}^{-3}$.

Rodot[3] has also given isoconcentration lines on a plot similar to Fig. 8. For a given temperature the value of p_{Hg} for intrinsic HgTe, $(p-n) = 0$, was assumed to be that at the minimum in a plot of $n^* = -6 \times 10^{18}/R_{77}$ against p_{Hg} . For equilibration at higher values of p_{Hg} it was assumed that all samples were n -type with $n^* = n = n - p$. Isoconcentration lines for intrinsic and n -type HgTe were constructed from the experimental data on the basis of these assumptions. Parameters obtained by a mass action law analysis of these lines were then used to calculate theoretical isoconcentration lines for p -type samples. These theoretical lines as well as the intrinsic line can be compared directly with our findings. The intrinsic line intersects the Hg-rich three-phase curve at 450°C. In disagreement we have found that HgTe that is Hg-saturated at 450°C is strongly p -type, with $(p-n) = (2 \pm 0.2) \times 10^{18} \text{ cm}^{-3}$. For $(p-n) = 4 \times 10^{18} \text{ cm}^{-3}$ and 315°C ($10^3/T = 1.70$), Rodot's theoretical analysis gives $p_{\text{Hg}} = 4.7 \times 10^{-3}$ atm. We obtain $p_{\text{Hg}} = 5.8 \times 10^{-4}$ atm, a factor of 8 lower (from Fig. 7 and the value of p_{Hg} along the Te-rich three-phase curve). As a result of these discrepancies we believe that considerable doubt is cast upon

Rodot's intrinsic line above 350°C and her analysis of the defect structure of HgTe at high temperatures.

Defect model for HgTe

In the preceding discussion it has been shown that there is a functional relationship between $(p-n)$ and x_{Te} in HgTe, but no microscopic model of the lattice defects responsible for this relationship has been considered. The simplest defect model assumes that $(p-n) = 0$ for $x_{\text{Te}} = \frac{1}{2}$ (stoichiometric material), that only one type of lattice defect is present, and that this is a simple point defect which is completely ionized to yield an integral number of carriers. Since in the experiments described above $(p-n)$ is always positive and increases as x_{Te} increases, according to this model it follows that the defects are acceptors and that all undoped p -type samples contain Te in excess of the stoichiometric composition. Furthermore the defects are either Hg vacancies or Te interstitials, although no data presently available make it possible to decide which. (The defects cannot be Te atoms on Hg sites, since these would be donors.)

If c is the number of holes per defect, which is expected to be 1 or 2,

$$p-n = c[A^{-c}] \quad (1)$$

where $[A^{-c}]$ is the concentration of defects. From the definition of atom fraction, it follows that

$$x_{\text{Te}} - \frac{1}{2} = \frac{(p-n)/2c}{2N \pm (p-n)/c} \quad (2)$$

where N is the concentration of lattice sites for each sublattice of the HgTe crystal, the plus sign in the denominator holds for Te interstitials, and the minus sign holds for Hg vacancies. Neglecting $(p-n)/c$ in comparison

with $2N$, equation (2) becomes for HgTe

$$x_{\text{Te}} - \frac{1}{2} = \frac{(p-n)}{c} (1.7 \times 10^{-23}) \quad (3)$$

since $N = 1.48 \times 10^{22} \text{ cm}^{-3}$ for HgTe ($a_0 = 6.46 \text{ \AA}$). From Fig. 7, the values of $(x_{\text{Te}} - \frac{1}{2})$ at the homogeneity limits are $(5.1 \times 10^{-5})/c$ and $(1.3 \times 10^{-4})/c$ for HgTe at 488°C . For $c = 1$ or 2 these values are consistent with the results of partial pressure measurements[2] which show that at this temperature the homogeneity limits lie within the range $-1 \times 10^{-3} < (x_{\text{Te}} - \frac{1}{2}) < +5 \times 10^{-3}$.

If the mass action law were applicable to the equilibrium between Hg vapor and HgTe containing defects, then for $p \gg n$, $(p-n)$ would be proportional to p_{Hg}^m , where $m = 1/(c+1)$. In this case the enthalpy of formation of a Hg-vacancy (or Te-interstitial) and c holes would be minus the partial enthalpy of Hg, about 43 kcal/g-atom . For the isotherm at 550°C plotted in Fig. 6, $m = 0.27$, in reasonably good agreement with the value of $\frac{1}{3}$ expected for $c = 2$. However, the mass action law is valid for equilibria involving holes and electrons only if the crystal is non-degenerate, i.e. if the Fermi level is located at least a few kT away from any energy band containing free carriers. It is unlikely that this condition is satisfied for HgTe, which is known to be a semi-metal at room temperature and below. Therefore it cannot be concluded with certainty that the acceptor defect in HgTe is doubly ionized. However, such behavior would not be surprising, since the acceptor defects in ZnTe[13] and SnTe[14] are known to be doubly ionized. (In our earlier study of the defect equilibria in HgSe[15], we analyzed the variation of carrier concentration with p_{Hg} in terms of a general equation which we believed to be applicable to equilibria involving degenerate as well as non-degenerate materials. However a recent statistical mechanical study[16] has indicated the need for correction terms which cannot be evaluated at present.)

Since our data show that even Hg-saturated

HgTe is p -type above 400°C , at least down to this temperature the entire homogeneity range of HgTe lies on the Te-rich side of the stoichiometric composition, according to the simple defect model given here. In order to account[17] for this behavior in terms of the thermodynamic properties of Hg, Te, and HgTe, at $x_{\text{Te}} = \frac{1}{2}$ the slope of the Gibbs free energy isotherms for HgTe above 400°C must be more negative than about -30 kcal/g-atom . This implies that the energy required to create the acceptor defect must be less than that required to create any defect associated with excess Hg by at least 30 kcal/g-atom . The existence of this large disparity is somewhat surprising, since none is observed for HgSe, whose homogeneity range lies entirely on the Hg-rich side of the stoichiometric composition.

Acknowledgements—The authors are grateful to A. E. Paladino for growing the HgTe crystals, to Mrs. M. C. Plonko for experimental assistance in annealing the samples and making electrical measurements, to J. M. Honig for making the Hall coefficient measurements at high magnetic fields, and to T. C. Harman for helpful discussions of the galvanomagnetic properties of HgTe.

REFERENCES

1. See review by HARMAN T. C., *Physics and Chemistry of II-VI Compounds* (Edited by M. Aven and J. S. Prener), Chap. 15. North-Holland, Amsterdam (1967).
2. BREBRICK R. F. and STRAUSS A. J., *J. Phys. Chem. Solids* **26**, 989 (1965).
3. RODOT H., *J. Phys. Chem. Solids* **25**, 85 (1964).
4. RODOT H., *C. r. Acad. Sci. Paris* **258**, 6386 (1964).
5. BREBRICK R. F. and ALLGAIER R. S., *J. chem. Phys.* **32**, 1826 (1960).
6. BREBRICK R. F. and GUBNER E., *J. chem. Phys.* **36**, 1283 (1962).
7. SCANLON W. W., *Phys. Rev.* **126**, 509 (1962).
8. STRAUSS A. J., *Trans. AIME* **239**, 794 (1967).
9. STRADLING R. A. and ANTCLIFFE G. A., *Proc. 8th Int. Conf. Physics of Semiconductors, Tokyo* (1966). (*J. phys. Soc. Japan Suppl.* **21**, 374 (1966)).
10. HARMAN T. C., HONIG J. M. and TRENT P., *J. Phys. Chem. Solids* **28**, 1995 (1967).
11. STRAUSS A. J., HARMAN T. C., MAVROIDES J. G., DICKEY D. H. and DRESSELHAUS M. S., *Proc. Int. Conf. Physics of Semiconductors, Exeter*, p. 703ff. Institute of Physics and The Physical Society, London (1962).

12. GIRIAT W., *Br. J. appl. Phys.* **15**, 151 (1964).
13. THOMAS D. G. and SADOWSKI E. A., *J. Phys. Chem. Solids* **25**, 395 (1964).
14. BREBRICK R. F. and STRAUSS A. J., *J. chem. Phys.* **41**, 197 (1964).
15. BREBRICK R. F. and STRAUSS A. J., *II-VI Semiconducting Compounds* (Edited by D. G. Thomas), p. 425. Benjamin, New York (1967).
16. BREBRICK R. F., *J. Solid State Chem.* **1**, 88 (1969).
17. BREBRICK R. F., *Progress in Solid State Chemistry* (Edited by H. Reiss), Vol. 3, p. 226. Pergamon Press, Oxford (1966).

***g*-FACTOR AND EFFECTIVE MASS OF ELECTRONS IN THE CONDUCTION AND THE VALENCE BANDS OF CuCl**

M. A. KHAN

Laboratoire de Physique des Solides*, Institut de Physique, 3, rue de l'Université, Strasbourg, France

(Received 7 October 1969; in revised form 13 January 1970)

Abstract—*g*-factors and effective masses of electrons are computed for the conduction and the valence bands of CuCl at the centre of the Brillouin Zone. The numerical values $g = 2.03$ for the conduction band, $g = -1.44$ for the upper valence band Γ_7^+ and the effective mass $m = -13.5$ a.u. for Γ_7^+ are in good agreement with the values deduced from the experiments on the excitonic states. For the second valence band Γ_8^+ , the numerical value calculated for g is 0.28.

1. INTRODUCTION

RECENT experiments of excitonic Zeeman effect in a strong magnetic field have permitted Certier[1] to obtain the values of the gyromagnetic factors of the electrons in the conduction and the higher valence bands of CuCl. It was interesting to see if these values were consistent with the theoretical values obtained from the Band Structure of CuCl[2]. In fact certain ambiguity could exist in the choice of the values deduced from the experiments. For example, the solution may not be unique, which is the case for a singlet state which is displaced quadratically in a magnetic field and in this case it is the square of the difference of the *g*-factors for electron and hole which comes into play. On the other hand certain hypotheses difficult to ascertain may be necessary to adopt, as is the case to explain the Zeeman spectra of the exciton complexes.

A direct calculation of *g*-factor from the band structure of CuCl permits us to remove these ambiguities and permits a certain justification of the model adopted by Certier for the exciton complexes that he has studied.

CuCl has a zinc-blende structure and Song [2] has calculated its band structure which we reproduce here in Fig. 1. The lowest

conduction band is Γ_1 and the highest valence band is Γ_{15}^+ , with spin-orbit interaction Γ_1 becomes two-fold degenerate Γ_6^+ while Γ_{15}^+ splits into two bands Γ_7^+ (two-fold degenerate) and Γ_8^+ (four-fold degenerate). These two valence bands give rise to two types of excitons named as fine and diffuse series[3].

As the valence band is degenerate and the conduction band is not (without spin orbit coupling), we had to adopt two different procedures for the calculation of the *g*-factors which we give in Section 2.

As the matrix elements required to calculate the effective mass are the same as that for *g*, it was interesting to calculate directly the effective mass of the valence band Γ_7^+ . Song[4] estimated this effective mass from the curvature of the dispersion curve. The high value of the effective mass at the top of the valence band explains the strong exciton phonon coupling observed[5]. We give the effective mass calculations in Section 3.

2. *g*-FACTOR

g-Factor for the electron in the conduction band

Roth[6] has shown that the *g*-factor for a two-fold degenerate band (including spin) can be obtained from the effective mass approximation. The effective mass Hamiltonian in the presence of a magnetic field is

*Equipe de Recherches sur la structure électronique des Solides associée au CNRS (No. 100).

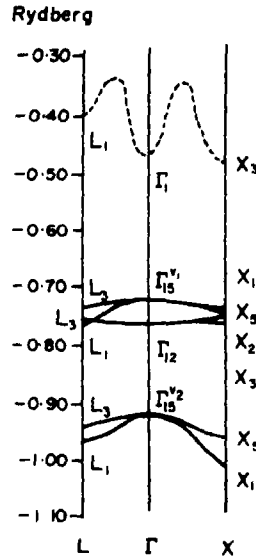


Fig. 1. Band structure of CuCl[2, 4]

$$H_{ij} = \frac{p^2}{2m} \delta_{ij} + 2u_B(\bar{S})_{ij} \cdot \bar{H} + \frac{1}{m^2} \sum_n \frac{\bar{P} \cdot \bar{\Pi}_{in} \bar{\Pi}_{nj} \cdot \bar{P}}{\epsilon_{0n}} \quad (1)$$

where $\bar{P}$ includes the momentum operator $\bar{p}$ and the vector potential $\bar{A}$, $(\bar{S})_{ij}$ is the matrix element of the electron spin between the i th and the j th band edge wave functions, u_B is the Bohr's magneton and

$$\bar{\Pi} = \bar{p} + (\hbar \bar{S} \times \bar{\nabla} V) / 2mc^2. \quad (2)$$

It is the third term of the equation (1) which gives the expressions for the effective mass and the g -factor. The equation for g -factor is:

$$\bar{\sigma}_{ij} \cdot \bar{g} = 4(\bar{S})_{ij} + \frac{2}{im} \sum_n \frac{\bar{\Pi}_{in} \times \bar{\Pi}_{nj}}{\epsilon_{0n}} \quad (3)$$

where $\bar{\sigma}$ is the Pauli spin vector and ϵ_{0n} stands for the energy difference between the states 0 and n . For small spin-orbit interaction

$$H_{s0} = \frac{\hbar}{2m^2 c^2} \bar{S} \cdot \bar{\nabla} V \times \bar{p} = 2\bar{S} \cdot \bar{h} \quad (4)$$

is considered only to the first order and $\bar{\Pi}$ is replaced by $\bar{p}$ and hence the above expression for g is reduced to

$$\bar{g} = 2\mathbf{I} + \frac{2}{mi} \sum_{uv} \frac{1}{\epsilon_{0u}\epsilon_{0v}} \{ \bar{h}_{0u} \bar{p}_{uv} \times \bar{p}_{v0} + \bar{h}_{uv} \bar{p}_{0u} \times \bar{p}_{v0} + \bar{h}_{v0} \bar{p}_{0u} \times \bar{p}_{uv} \} \quad (5)$$

which is a matrix equation with $\mathbf{I}$ as a unit matrix, u and v as the intermediate states and 0 as the band edge under consideration.

The conduction band under consideration has the symmetry of Γ_1 , where as the nearest valence bands are of Γ_{15} and Γ_{12} symmetry. More remote bands are neglected in this calculation. Operator $\bar{h}$ is of Γ_{15} symmetry so it can be seen right away that

$$\bar{h}_{0u} = \bar{h}_{0v} = 0 \quad (6)$$

because

$$\langle \Gamma_1 | \Gamma_{15} | \Gamma \rangle = 0 \quad \text{for } \Gamma \neq \Gamma_{15}.$$

So only the middle term in the curly bracket of equation (5) is non-zero. We are left with three neighbouring valence bands, two of them having the symmetry of Γ_{15} and one of Γ_{12} . $\bar{p}$ has the symmetry of Γ_{15} . Therefore $\bar{p}_{0u} = \langle \Gamma_1 | \Gamma_{15} | \Gamma \rangle$ is non-zero only when $\Gamma = \Gamma_{15}$. We conclude that Γ_{12} gives no contribution.

For a particular axis z we can write the equation (5) as

$$\begin{aligned} g_{zz} - 2 = & Re \frac{4}{mi} \frac{1}{(\epsilon_{\Gamma_1}, \Gamma_{15}^v)^2} \{ \langle \Gamma_{15}^{v_{1z}} | h_z | \Gamma_{15}^{v_{1z}} \rangle \\ & \times \langle \Gamma_1 | p_x | \Gamma_{15}^{v_{1x}} \rangle \langle \Gamma_{15}^{v_{1x}} | p_y | \Gamma_1 \rangle \} \\ & + Re \frac{4}{mi} \frac{1}{(\epsilon_{\Gamma_1}, \Gamma_{15}^v)^2} \{ \langle \Gamma_{15}^{v_{1z}} | h_z | \Gamma_{15}^{v_{1z}} \rangle \\ & \times \langle \Gamma_1 | p_x | \Gamma_{15}^{v_{1x}} \rangle \langle \Gamma_{15}^{v_{1x}} | p_y | \Gamma_1 \rangle \} \\ & + Re \frac{8}{mi} \frac{1}{(\epsilon_{\Gamma_1}, \Gamma_{15}^v)(\epsilon_{\Gamma_1}, \Gamma_{12}^v)} \langle \Gamma_{15}^{v_{1z}} | h_z | \Gamma_{15}^{v_{1z}} \rangle \\ & \times \langle \Gamma_1 | p_x | \Gamma_{15}^{v_{1x}} \rangle \times \langle \Gamma_{15}^{v_{1x}} | p_y | \Gamma_1 \rangle \} \quad (7) \end{aligned}$$

'Re' stands for 'real part of'.

We calculated

$$\left. \begin{aligned} 2i \langle \Gamma_{15}^{v_{1z}} | h_z | \Gamma_{15}^{v_{1z}} \rangle &= a_1^2 \xi_{3p} - b_1^2 \xi_{3d} = -0.0027 \\ &\text{a.u. (Energy)} \\ 2i \langle \Gamma_{15}^{v_{1y}} | h_z | \Gamma_{15}^{v_{1y}} \rangle &= a_2^2 \xi_{3p} - b_2^2 \xi_{3d} = -0.0021 \\ &\text{a.u. (Energy)} \\ 2i \langle \Gamma_{15}^{v_{1x}} | h_z | \Gamma_{15}^{v_{1x}} \rangle &= a_1 a_2 \xi_{3p} - b_1 b_2 \xi_{3d} = -0.0027 \\ &\text{a.u. (Energy)} \end{aligned} \right\} \quad (8)$$

These expressions are nothing but spin-orbit splittings of different bands and

$$\left. \begin{aligned} |\Gamma_{15}^{v_{1z}}\rangle &= a_1 \Psi_{3p}^x(\text{Cl}^-) + b_1 \Psi_{3d}^{yz}(\text{Cu}^+) = \epsilon_1 \\ |\Gamma_{15}^{v_{1y}}\rangle &= a_1 \Psi_{3p}^y(\text{Cl}^-) + b_1 \Psi_{3d}^{xz}(\text{Cu}^+) = \epsilon_2 \\ |\Gamma_{15}^{v_{1x}}\rangle &= a_1 \Psi_{3p}^z(\text{Cl}^-) + b_1 \Psi_{3d}^{xy}(\text{Cu}^+) = \epsilon_3 \end{aligned} \right\} \quad (9)$$

and

$$\left. \begin{aligned} |\Gamma_{15}^{v_{1z}}\rangle &= a_2 \Psi_{3p}^x(\text{Cl}^-) + b_2 \Psi_{3d}^{yz}(\text{Cu}^+) = \delta_1 \\ |\Gamma_{15}^{v_{1y}}\rangle &= a_2 \Psi_{3p}^y(\text{Cl}^-) + b_2 \Psi_{3d}^{xz}(\text{Cu}^+) = \delta_2 \\ |\Gamma_{15}^{v_{1x}}\rangle &= a_2 \Psi_{3p}^z(\text{Cl}^-) + b_2 \Psi_{3d}^{xy}(\text{Cu}^+) = \delta_3 \end{aligned} \right\} \quad (10)$$

$$|a_i|^2 + |b_i|^2 = 1. \quad (11)$$

These coefficients have been calculated by Song during Band Structure calculation of CuCl[7] and their values are as follows:

$$\begin{aligned} a_1 &= -0.4585, b_1 = 0.8887 \\ a_2 &= 0.9324, b_2 = 0.3620 \end{aligned}$$

$x, y, z, yz, zx,$ and xy represent the symmetries of the atomic states. $\Psi_{3p}(\text{Cl}^-)$ and $\Psi_{3d}(\text{Cu}^+)$

$$\left| \begin{array}{ccc|ccc} H_{11} - W & H_{13} & H_{16} & & & \\ H_{13}^* & H_{11} - W & H_{36} & & & \\ H_{16}^* & H_{36}^* & -H_{11} - W & & & \\ & & & 0 & & \\ & & & & -H_{11} - W & H_{24} \\ & & & & H_{24}^* & -H_{11} - W \\ & & & & H_{25} & H_{45}^* \end{array} \right| = 0 \quad (15)$$

are the atomic functions of Cl^- and Cu^+ for $3p$ and $3d$ bands respectively [8].

ξ_{3p} and ξ_{3d} are the atomic spin-orbit couplings for $3p$ of Cl^- and $3d$ of Cu [9].

The matrix elements of the operator $\bar{p}$ and the energy differences ϵ 's are known from Song's [2] calculations. Substituting these values in equation (7) we obtain

$$g_{zz} \approx 2.03. \quad (12)$$

As CuCl has a cubic symmetry g -factor is expected to be the same in any direction. This result is in agreement with the experimental value obtained by Certier.

g-factor for electron in the valence band Γ_{15}^v

As mentioned before the valence band is degenerate in the absence of spin orbit coupling so the above method could not be applied for this band. In the presence of the spin-orbit coupling and a magnetic field the total perturbation can be written as [10]

$$H' = \xi(r) \bar{S} \cdot \bar{L} + \frac{1}{\hbar} \mu_B \bar{H} \cdot (\bar{L} + 2\bar{S}). \quad (13)$$

We consider the effect of this perturbation on the unperturbed states of Γ_{15}^v including the spin. These states are

$$\Phi_j = \epsilon_i \gamma \quad (14)$$

$$j = 1, 2, \dots, 6 \quad \text{and } i = 1, 2, 3$$

$$\gamma = \alpha, \beta \text{ (the spin wave vectors).}$$

We calculated the different matrix elements for the perturbation operator H' and obtained a 6×6 secular equation.

$$H_{ij} = \langle \Phi_i | H' | \Phi_j \rangle. \quad (16)$$

Secular equation (15) can be diagonalized and the diagonalized representations in $|J, m_j\rangle$ notation are

$$\begin{aligned} \left| \frac{1}{2}, \frac{1}{2} \right\rangle &= \frac{1}{\sqrt{3}} \{ \epsilon_3 \alpha + (\epsilon_1 + i\epsilon_2) \beta \} = |1\rangle \\ \left| \frac{1}{2}, -\frac{1}{2} \right\rangle &= \frac{1}{\sqrt{3}} \{ \epsilon_3 \beta - (\epsilon_1 - i\epsilon_2) \alpha \} = |2\rangle \\ \left| \frac{3}{2}, \frac{3}{2} \right\rangle &= \frac{1}{\sqrt{2}} (\epsilon_1 + i\epsilon_2) \alpha = |3\rangle \\ \left| \frac{3}{2}, \frac{1}{2} \right\rangle &= \frac{1}{\sqrt{6}} \{ 2\epsilon_3 \alpha - (\epsilon_1 + i\epsilon_2) \beta \} = |4\rangle \\ \left| \frac{3}{2}, -\frac{1}{2} \right\rangle &= \frac{1}{\sqrt{6}} \{ 2\epsilon_3 \beta + (\epsilon_1 - i\epsilon_2) \alpha \} = |5\rangle \\ \left| \frac{3}{2}, -\frac{3}{2} \right\rangle &= \frac{1}{\sqrt{2}} \{ (\epsilon_1 - i\epsilon_2) \beta \} = |6\rangle. \end{aligned} \quad (17)$$

From secular equation (15) we get the following energy equations:

$$E = E_0 + 2A + m_1 g_1 \mu_B H \quad (18)$$

where

$$m_1 = \pm \frac{1}{2} \text{ and } g_1 = -1.44 \quad (19)$$

and

$$E = E_0 - A + m_2 g_2 \mu_B H \quad (20)$$

where

$$m_2 = \pm \frac{3}{2}, \pm \frac{1}{2} \text{ and } g_2 = 0.28. \quad (21)$$

E_0 is the eigenvalue of the ground state. In the absence of a magnetic field (i.e. $H = 0$)

the spin-orbit coupling splits the degenerate Γ_{15}^V valence band into two states Γ_7^+ and Γ_8^+ . The state Γ_7^+ is two-fold degenerate and these two degenerate states are represented in equation (17) as $|\frac{1}{2}, \frac{1}{2}\rangle$ and $|\frac{1}{2}, -\frac{1}{2}\rangle$. The state Γ_8^+ is four-fold degenerate and is represented by the states $|\frac{3}{2}, \frac{3}{2}\rangle$, $|\frac{3}{2}, \frac{1}{2}\rangle$, $|\frac{3}{2}, -\frac{1}{2}\rangle$, and $|\frac{3}{2}, -\frac{3}{2}\rangle$ in equation (17). From the representation of Γ_7^+ and Γ_8^+ it is seen that Γ_7^+ lies above Γ_8^+ such that

$$\begin{aligned} \Delta E &= E(\Gamma_8^+) - E(\Gamma_7^+) = -3A \\ &= -0.0041 \text{ a.u. (energy)}. \end{aligned} \quad (22)$$

The spin-orbit splitting ΔE is in agreement with the value calculated by Song[4].

It is seen that in a magnetic field Γ_7^+ is split into two lines such that $|\frac{1}{2}, -\frac{1}{2}\rangle$ lies above $|\frac{1}{2}, \frac{1}{2}\rangle$ which means g factor is negative i.e. $g_1 = -1.44$ which is quite comparable with the value obtained by Certier[1] as -1.2 ± 0.1 . Γ_8^+ band is split in a magnetic field into four levels such that $|\frac{3}{2}, \frac{3}{2}\rangle$ is the highest and $|\frac{3}{2}, \frac{1}{2}\rangle$, $|\frac{3}{2}, -\frac{1}{2}\rangle$, $|\frac{3}{2}, -\frac{3}{2}\rangle$ follow in descending order which gives g_2 with a positive sign i.e., $g_2 = 0.28$. Figure 2 represents the splitting of Γ_{15}^V under spin-orbit coupling and magnetic field.

As we know the correct representation for Γ_7^+ we can apply equation (3) directly to calculate the value of g for this doubly degenerate band. The two representations are equivalent. We take the state

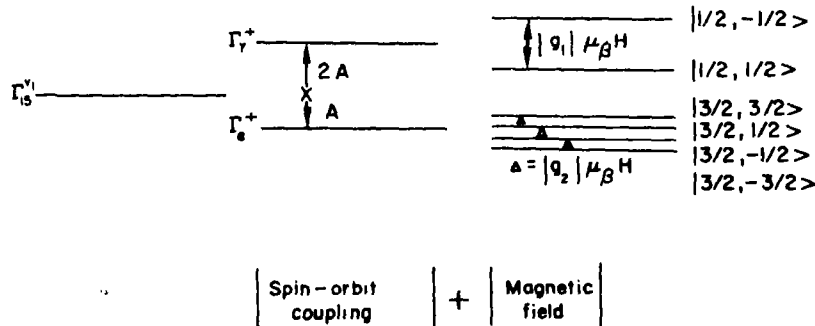


Fig. 2. Splitting of the valence band Γ_{15}^V under spin-orbit coupling and magnetic field. $A = 0.00136$ a.u., $g_1 = -1.44$, $g_2 = 0.28$ for $|J, m_j\rangle$ representation see the text.

$$\frac{1}{\sqrt{3}} [\epsilon_3 \alpha + (\epsilon_1 + i\epsilon_2) \beta] = |1\rangle$$

$$\lambda_k = E_k - \frac{\hbar^2 k^2}{2m} \quad (26)$$

for our calculation.

For a small spin-orbit interaction equation (3) can be written as:

$$g_{zz} = 2 - Re \frac{12}{im} \sum_n \frac{\langle 1|p_x|n\rangle \langle n|p_y|1\rangle}{E_1 - E_n} \quad (3a)$$

the neighbouring band edges $|n\rangle$ are Γ_1 , Γ_{12} and Γ_{15}^v as shown in Fig. 1, taking the double group representations [11] for the neighbouring band edges

$$\sum_n \frac{\langle 1|p_x|n\rangle \langle n|p_y|1\rangle}{E_1 - E_n} = 0.28$$

and equation (3a) gives the value of $g = -1.36$ which is not much different from the value previously calculated by perturbation method. It shows that the effect of the neighbouring intermediate states $|n\rangle$ is very small.

3. EFFECTIVE MASS

Effective mass of the electrons in the conduction and the valence bands

Spin-orbit coupling effects in zinc-blende structure have been already treated by Dresselhaus [11]. Schrödinger equation with spin-orbit coupling is:

$$\left[\frac{p^2}{2m} + V + \frac{\hbar}{4m^2 c^2} (\bar{\nabla} V \times \bar{p}) \cdot \bar{\sigma} \right] \Psi_k = E_k \Psi_k \quad (23)$$

$\Psi_k(r)$ is of Bloch form i.e.

$$\Psi_k(r) = U_k(r) e^{ik \cdot r} \quad (24)$$

where $U_k(r)$ is periodic and satisfies the equation

$$\left[\frac{p^2}{2m} + V + \frac{\hbar}{4m^2 c^2} (\bar{\nabla} V \times \bar{p}) \cdot \bar{\sigma} \right] U_k + \hbar \bar{k} \cdot \left(\frac{\bar{p}}{m} + \frac{\hbar}{4m^2 c^2} \sigma \times \bar{\nabla} V \right) U_k = \lambda_k U_k \quad (25)$$

In the equation (25) the term

$$H_1 = \frac{\hbar}{m} \bar{k} \cdot \left(\bar{p} + \frac{\hbar}{4m c^2} \sigma \times \bar{\nabla} V \right) \quad (27)$$

is treated as a perturbation.

Song [4] has calculated the value of the effective mass of the conduction electron by this method, so we shall limit ourselves to the calculation of the effective mass of the valence electron only.

The diagonalized representations of Γ_7^+ and Γ_8^+ (from Γ_{15}^v) are given in equation (17). The diagonalized state for the neighbouring bands Γ_1 , Γ_{15}^v and Γ_{12} are also known [11].

Effective mass of the electron in Γ_7^+ band

To the first order of perturbation we see that H_1 gives no contribution. For the second order calculations we consider the first term in the perturbation to be more important [6] and hence we shall consider only the term $\hbar \bar{k} \cdot \bar{p}/m$. For Γ_7^+ we obtain a secular determinant as

$$\begin{vmatrix} Dk^2 - \lambda & 0 \\ 0 & Dk^2 - \lambda \end{vmatrix} = 0 \quad (28)$$

where D is a constant such that

$$Dk^2 = \sum_j \frac{\langle 1|H_1|j\rangle \langle j|H_1|1\rangle}{E_1 - E_j} \quad (29)$$

where $|1\rangle$ is any of the two representations of Γ_7^+ and $|j\rangle$ are the intermediate states (i.e. Γ_1 , Γ_{15}^v and Γ_{12}).

From equation (28) we obtain

$$\begin{aligned} E(k) &= \frac{k^2}{2} + \lambda \\ &= \frac{k^2}{2m^*} \quad (\text{in a.u.}) \end{aligned} \quad (30)$$

and we get $m^* = -13.5 \text{ a.u.}$ as the effective

mass of the electron in Γ_7^+ band. This is in agreement with the value estimated by Song [4] also obtained as isotropic mass as we do here.

Effective mass of the electrons in Γ_8^+

The first order effect of the perturbation comes only from the second part of the expression 27 and the secular equation is similar to that given by Dresselhaus [11]

$$\begin{vmatrix} -\lambda & -Ck_+ & 2Ck_z & -\sqrt{3}Ck_- \\ -Ck_- & -\lambda & -\sqrt{3}Ck_+ & 2Ck_z \\ 2Ck_z & -\sqrt{3}Ck_- & -\lambda & Ck_+ \\ -\sqrt{3}Ck_+ & 2Ck_z & Ck_- & -\lambda \end{vmatrix} = 0 \quad (31)$$

which gives

$$E_k = \frac{\hbar^2 k^2}{2m} \pm 2C[k^2 \pm \sqrt{3}(k_x^2 k_y^2 + k_y^2 k_z^2 + k_z^2 k_x^2)^{1/2}]^{1/2} \quad (32)$$

where

$$k_+ = k_x + ik_y \text{ and } k_- = k_x - ik_y$$

and

$$C = \frac{1}{\sqrt{3}} \frac{\hbar^2}{4m^2 c^2} \left\langle \epsilon_1 \left| \frac{\partial V}{\partial y} \right| \epsilon_3 \right\rangle. \quad (33)$$

For the zinc-blende structure Dresselhaus [11] has shown that

$$2C = -\frac{\Delta_{80} \times a}{Z} \quad (34)$$

where Δ_{80} is the spin-orbit splitting of the valence band Γ_{15}^+ , a , the lattice constant and Z the atomic number. As the factor Δ_{80} is very small (see Section 2 of this article), the value of C also turns out to be very small (of the order of 10^{-4}) and hence for small values of k there will be almost no first order correction in the energy level expressed by relation (32), so that the top of the band will remain very close to the centre of the Brillouin Zone.

For the second order perturbation we consider only the term $\hbar/m \bar{k} \cdot \bar{p}$ as before and we get a 4×4 determinant.

$$\begin{vmatrix} H_{33} - \lambda & H_{34} & H_{35} & 0 \\ H_{34}^* & H_{44} - \lambda & 0 & -H_{35} \\ H_{35}^* & 0 & H_{44} - \lambda & H_{34} \\ 0 & -H_{35}^* & H_{34}^* & H_{33} - \lambda \end{vmatrix} = 0 \quad (35)$$

which simplifies to a quadratic equation

$$\lambda^2 - (H_{33} + H_{44})\lambda + (H_{33}H_{44}) - |H_{34}|^2 - |H_{35}|^2 = 0 \quad (36)$$

$$H_{1n} = \sum_j \frac{\langle 1 | \frac{\hbar}{m} \bar{k} \cdot \bar{p} | j \rangle \langle j | \frac{\hbar}{m} \bar{k} \cdot \bar{p} | n \rangle}{E_1 - E_j} \quad (37)$$

$|1\rangle$ and $|n\rangle$ are any of the four representations of Γ_8^+ and $|j\rangle$ the intermediate states (i.e. $\Gamma_1, \Gamma_{15}^{V_2}$ and Γ_{12}).

Energy equation can also be written as

$$E(k) = Ak^2 \pm [B^2 k^4 + C^2 (k_x^2 k_y^2 + k_y^2 k_z^2 + k_z^2 k_x^2)]^{1/2} \quad (38)$$

where

$$A = \frac{1}{3}(L + 2M) + \frac{1}{2} = -0.1045$$

$$B = \frac{1}{3}(L - M) = -0.0681$$

and

$$C^2 = \frac{1}{3}[N^2 - (L - M)^2] = -0.0135.$$

L , M and N are the same matrix elements as defined by Dresselhaus *et al.* [12] and their numerical values calculated for CuCl are:

$$L = -0.7407$$

$$M = -0.5364$$

$$N = -0.0364.$$

For $\bar{k} = k[100]$, we get two effective masses as

$$m^* = -13.7 \text{ and } -3 \text{ a.u.}$$

Similarly for $\bar{k} = k/\sqrt{2} [110]$, effective masses are -7.2 and -3.6 a.u. and for $\bar{k} = k/\sqrt{3} [111]$, effective masses are -10.3 and -3.1 a.u. From our results we conclude that in the band Γ_8^+ , the effective mass of the elec-

tron defined in a given direction of $\vec{k}$ by the relation $(1/m^*) = (\partial^2 E(k)/\partial k^2)$ (in a.u.), is anisotropic and it lies anywhere in between -3 and -13.7 a.u. depending upon the direction of $\vec{k}$.

Considering the diffuse exciton series[3] as hydrogen like and permitting ourselves to use the small effective mass approximation, from two extreme values of the effective mass of the hole we obtain that the first line of this series could lie anywhere in between 3789 and $3818 \text{ \AA}$. The value $3785 \text{ \AA}$ given by Ringeissen[5] is well within this range. It is interesting to note that the calculated energy difference $29 \text{ \AA}$ is comparable with the experimental value of the line width of the first line of the diffuse exciton series[3].

Acknowledgements—This work was performed under the guidance of Professor E. Daniel, director of the Laboratory of Physics of Solids and his constant help is gratefully acknowledged.

My thanks are due to Drs. K. S. Song and M. Certier for many useful discussions and particularly to Dr. K. S.

Song for supplying me the unpublished numerical values of a 's and b 's.

REFERENCES

1. CERTIER M., WECKER C. and NIKITINE S., *9th Int. Conf. Phys. Semi-conductors, Moscou*, pp. 1, 466 (1968).
CERTIER M., Thesis, Univ. of Strasbourg (1969).
CERTIER M., WECKER C. and NIKITINE S., *J. Phys. Chem. Solids* **30**, 2135 (1969).
2. SONG K. S., *J. Phys., Paris* **28**, 195 (1967).
3. NIKITINE S. and RINGEISSEN J., *J. Phys., Paris* **26**, 171 (1965).
4. SONG K. S., *J. Phys., Paris* **28**, C3-43 (1967).
5. RINGEISSEN J., CORET A. and NIKITINE S., *Conf. Localized Excitons in Solids, Irvine*, p. 297 (1968).
6. ROTH L. M., *Phys. Rev.* **118**, 1534 (1960).
7. SONG K. S., Private communication
8. HARTREE D. R. and HARTREE W., *Proc. R. Soc.* **156A**, 45 (1936).
HARTREE D. R. and HARTREE W., *Proc. R. Soc.* **157A**, 490 (1936).
9. SONG K. S., *J. Phys. Chem. Solids* **28**, 2003 (1967).
10. SCHIFF L., *Quantum Mechanics*, p. 293. McGraw-Hill, New York (1955).
11. DRESSELHAUS G., *Phys. Rev.* **100**, 580 (1955).
12. DRESSELHAUS G., KIP A. F. and KITTEL C., *Phys. Rev.* **98**, 368 (1955).

BAND STRUCTURE OF SILICON BY PSEUDO-OPW

A. K. HOCHBERG* and C. R. WESTGATE

Johns Hopkins University, Baltimore, Md. 21218, U.S.A.

(Received 29 December 1969)

Abstract—A modification of the procedure for calculating electronic energy band structures by the Orthogonalized Plane Wave method has been applied to silicon. An analytic set of core and valence electron wave functions for an sp^3 configuration of silicon has been obtained self-consistently and yields atomic scattering factors in close agreement with experimental values. This result is then used to improve the valence electron contribution to the potential used in the OPW calculations. This contrasts with the use of adjustments to experimental transition energies used in recent perturbed OPW calculations. The band structure determination has produced transition energies, effective mass parameters, and deformation potentials in good agreement with experimental values and with perturbed OPW calculations.

1. INTRODUCTION

SINCE Herman[1] and Woodruff[2] extended Herring's[3] method of Orthogonalized Plane Waves (OPW) to valence crystals, there have been several such calculations on diamond-type semiconductors. These first-principles calculations have not always been successful in producing results consistent with experimental evidence[4]. Although the OPW method requires that an emphasis be placed on obtaining a self-consistent potential for valence electrons, there is insufficient evidence to show that such a result is representative of the actual field in a crystal. It is our intention to show that reasonable results may be obtained for silicon without employing a completely self-consistent procedure.

Since a nearly self-consistent potential for diamond-type crystals results from simply superimposing free atom potentials[5], emphasis has been placed upon obtaining an accurate description of the core states, described in Section 2. This result provides a spherically-symmetric approximation to the crystal potential and is employed in the OPW calculations of Section 3. The distortion of the spherical symmetry due to the tetrahedral

bonding between atomic sites is taken into account by correction terms in a manner similar to that of Herman *et al.*[4] in Section 4. However, Herman has adjusted to experimental transition energies, while our perturbing terms, with values of the same order of magnitude as corrections obtained in self-consistent valence potential procedures, are associated with atomic scattering factors.

The methods of Brooks[6] and Kleinman and Phillips[7] which account for correlation and exchange have been employed to modify the ' $\rho^{1/3}$ exchange' of Slater[8]. The calculated transition energies compare favorably with experiment and with Herman's results. In addition, effective mass parameters obtained from the band structure and calculated deformation potentials also agree with experimental results, as shown in Sections 5 and 6.

2. CORE STATES

For OPW calculations it is necessary to maintain an internal consistency in which all core, valence, and conduction electron wave functions are eigenfunctions of the same Hamiltonian. Under this restriction analytic core state wave functions associated with an sp^3 valence configuration, characteristic of atoms in the crystal, are obtained in a self consistent scheme. The atomic potential

*Present address: KDI Poly-Technic, Cincinnati, Ohio 45215, U.S.A.

derived from these functions is then used in the OPW procedure.

The core state wave functions, $\xi_{nlm}(\bar{r})$, are solutions of the free atom Schrödinger equation

$$H(\bar{r}, l) \xi_{nlm}(\bar{r}) = (-\nabla^2 - V_A(\bar{r}) + l(l+1)/r^2) \xi_{nlm}(\bar{r}) = W_{nl}(\bar{r}) \xi_{nlm}(\bar{r}). \quad (1)$$

The atomic potential employed is of the form

$$V_A(\bar{r}) = -2Z/r + V_c(\bar{r}) + V_{EX}(\bar{r}), \quad (2)$$

where Z is the nuclear charge, the electronic coulomb term is

$$V_c(\bar{r}) = 2 \int d\bar{r}' \rho(\bar{r}') / |\bar{r} - \bar{r}'|. \quad (3)$$

The exchange term is

$$V_{EX}(\bar{r}) = -6[(3/8\pi)\rho(\bar{r})]^{1/3} \quad (4)$$

and the charge density is

$$\rho(\bar{r}) = \sum_{j=1}^{14} \xi_j^*(\bar{r}) \xi_j(\bar{r}). \quad (5)$$

Since the atomic potential is obtained from the charge distribution due to the $\xi_j(\bar{r})$, (1) is an integrodifferential equation which cannot be evaluated analytically. Solutions may be obtained by a method of successive approximations whose rapid convergence depends upon the initial approximations to the true wave functions. In determining the core states, spherically symmetric functions are used to describe the valence electrons. In the following OPW calculations, these valence wave functions are replaced by symmetrized combinations of plane waves orthogonalized to the core functions.

In the completely self-consistent band structure calculations the OPW valence functions are used to correct the core functions in succeeding iterations. Since these OPW functions are non-local (k -dependent), they must be obtained for many points in the Brillouin zone with suitable averaging to obtain a

local (r -dependent) potential for use in the core state calculations. This task is usually simplified by sampling only at high symmetry points where the secular determinant may be factored. This correction due to the small sampling, applied to the potential derived using spherically symmetric approximations to valence electron wave functions, may have errors comparable with values of the corrections [7, 9]. As noted above, a nearly self-sufficient potential is obtained for silicon using free atom functions, so all iterations to obtain the core state functions in our calculations did not involve OPW sampling.

The core functions are evaluated in the form

$$\xi_{nlm}(\bar{r}) = P_{nl}(r)/r Y_l^m(\theta, \phi) \quad (6)$$

where $Y_l^m(\theta, \phi)$ are normalized spherical harmonics, and the radial functions are

$$P_{nl}(r) = \sum_j a_j r^{n_j} \exp(-\sigma_j r). \quad (7)$$

Initially, the exponents, σ_j , are calculated according to Slater's [10, 11] rules in the manner of Woodruff [2]. Each function is orthogonalized to all inner core functions having the same l value, and the resulting charge density is used to obtain the starting potential, $V_A^{(j=0)}(r)$. In succeeding iterations the results of Löwdin [12, 13] are incorporated to decrease the arbitrariness in selecting exponents and coefficients for trial functions, $P_{nl}^{(j+1)}(r)$, to be substituted into

$$(-\nabla^2 + V_A^{(j)}(r) + l(l+1)/r^2 - E_{nl}^{(j)}) \times P_{nl}^{(j+1)}(r) = \Delta(r). \quad (8)$$

Here, $\Delta(r)$ is the misfit of the trial function at r and is zero for the correct eigenfunction. Exponent adjustments are made to minimize $\Delta(r)$ over the widest range of r for each trial function. Linearity rules determined by Löwdin relate self-consistent field core orbitals which appear sequentially in the Periodic Table. They are of the form

$$K_{nl} = [\alpha_{nl} P_{nl}(r)/r^{l+1}]_{r=0}^{2l(K2l+3)}, \quad (9)$$

and values used initially for effective nuclear charges, K_{nl} , and coefficients, α_{nl} , are those obtained by Löwdin. These values appear applicable to closed shells only and are not used for the spherical approximations to valence electron functions. Equation (9) controls a function in the region of the nucleus only, so additional node and maxima controls are imposed on the $2s$, $3s$ and $3p$ functions. These trial functions are differentiated and equated to zero in ranges of r values for which Herman and Skillman[14] obtained corresponding nodes and maxima for an s^2p^2 valence configuration. The best fits for the sp^3 configuration, according to [8], required maxima slightly farther from the origin than in corresponding Herman-Skillman functions.

The exchange potential used in the iteration scheme is a slightly modified ' $\rho^{1/3}$ exchange' approximation of Slater[8]. Heine[15] and Kleinman and Phillips[7] have suggested that averaged charge densities produce more realistic exchange potentials, since, for example, the variations of valence charge densities in the core region are screened by core electrons, so that the effective valence charge density is an average value in this region. Also, the non-local nature of the exchange interaction suggests that average densities rather than local oscillations produce more realistic exchange potentials, since this potential does not vary

as rapidly with r as do wave functions being calculated. For these reasons, an averaged valence charge density is employed in the core region and, in addition, the $2s$ charge density is averaged in the vicinity of its node for further emphasis. This averaging increases s -state energies and decreases those of p -states (energies are changed by approximately 0.1 per cent). This is due to a decrease in magnitude of the (attractive) exchange potential in the region where s -functions have their first maxima and to an increase, over un-averaged ' $\rho^{1/3}$ ' values, in regions of p -function maxima.

In Table 1, our calculated orbital energies, after four iterations, are compared with previous determinations for silicon. The present results are in close agreement with the Herman-Skillman values for an s^2p^2 valence configuration. The coefficients, C_{nlj} and D_{nmj} , and exponents, α_{nlj} , of our core functions in the form

$$P_{nl}(r) = r^n \sum_j C_{nlj} \exp(-\alpha_{nlj}r) - \sum_{m < n} D_{nmj} P_{mj} \quad (10)$$

are listed in Table 2.

The charge density, $\rho(r)$, produced by the calculated core functions, including the spherically symmetric approximations to the valence electron functions, may be compared with the experimental charge density in silicon using the atomic scattering factors, $f(\bar{H})$,

Table 1. Calculated orbital energies for silicon (in Rydbergs)

Herman and Skillman ^a	Kleinman and Phillips ^b	Quelle ^c	Woodruff ^d	Present results
$E_{1s} - 134.04$	-131.4208	-134.4208	-134.597	-133.918
$E_{2s} - 11.087$	-12.00415	-11.655	-11.1237	-11.1075
$E_{2p} - 7.954$	-8.72145	-8.516	-8.17697	-7.9829
$E_{3s} - 0.9975$				-0.99028
$E_{3p} - 0.4802$				-0.45645

^aValence configurations s^2p^2 , Ref. [14], vs. sp^3 for other columns.

^bHartree Si^{4+} core, Ref. [7].

^cRef. [9].

^dRef. [2].

Table 2. Core function coefficients and exponents

	1s	2s	2p	3s	3p
C_{n11}	53.6933	35.6981	34.7573	0.6046	0.5654
C_{n12}	48.3805	92.8656	54.2235	3.2817	2.1569
C_{n13}	—	-119.8169	—	—	—
α_{n11}	12.17	4.275	4.25	1.45	1.20
α_{n12}	16.10	7.60	8.30	2.00	2.10
α_{n13}	—	10.20	—	—	—
D_{211}	—	0.2735	—	—	—
D_{311}	—	—	—	-0.0820	—
D_{321}	—	—	—	0.3419	0.2433

obtained from X-ray investigations. The theoretical factors are calculated from

$$f(\bar{H}) = 4\pi \int_0^\infty \rho(r)r^2 \sin(|\bar{H}|r)/(|\bar{H}|r) dr, \quad (11)$$

where $\bar{H} = 2\pi a^{-1}(h_1, h_2, h_3)$. The present results are compared in Table 3 with factors calculated from the data of Kleinman and Phillips[6] and recent experimental values of DeMarco and Weiss[16], as corrected by Dawson[17], which are appropriate for stationary atoms. It appears that the calculated charge density is in reasonable agreement with these experimental determinations. For lowest $\bar{H}$ values, the difference between theoretical and experimental $f(\bar{H})$ values may be attributed to the deviations from spherical sym-

metry of the valence electron charge density in the crystal. Corrections are made for these deviations in the band structure calculation of Section 4.

3. OPW CALCULATIONS

The valence and conduction states of silicon are calculated by the OPW method at many points in the Brillouin zone using approximately 125 OPW's per point. Due to the relatively small number of OPW's employed convergence is not obtained, although the indirect band gap energy changes by less than 0.001 Ry for 137 vs. 125 OPW's.

Brook's non-local exchange-correlation hole[6] is used to modify the Fourier coefficients of the valence-valence exchange, $v_x^{\text{val-val}}(\bar{H})$, so that smaller percentages of these coefficients are used with increasing $\bar{H}$. The Brooks' relation is given by

$$v_{\text{Brooks}}^{\text{val-val}}(H) = v_x^{\text{val-val}}(\bar{H}) \times 2.9738 [(1 + \rho_0^2 H^2)^{-1} + 0.667 (1 + \rho_0^2 H^2)^{-2}], \quad (12)$$

where ρ_0 is an average radius of the exchange hole and is equal to $0.55 v_s$ in silicon; v_s is the radius of the average volume per valence electron. To account for the momentum dependence of this valence-valence exchange, $\frac{4}{3}v_{\text{Brooks}}^{\text{val-val}}(\bar{H})$ values are used for states associated with the lowest valence bands (Γ_1, X_1, L_1, L_2) and $\frac{2}{3}v_{\text{Brooks}}^{\text{val-val}}(\bar{H})$ values are employed for other states in the manner of Kleinman and Phillips[7].

Table 3. Comparison of theoretical and experimental scattering factors for silicon

h_1, h_2, h_3	DeMarco and Weiss ^a	Kleinman and Phillips ^b	Present results
111	10.81 ± 0.08	10.32	10.67
220	8.71 ± 0.06	8.29	8.81
311	8.08 ± 0.08	7.96	8.26
400	7.70 ± 0.08	7.35	7.61
331	7.42 ± 0.10		7.29
422	6.84 ± 0.10		6.82
333	6.51 ± 0.08	6.20	6.56
511	6.57 ± 0.09		
440	6.06 ± 0.08		6.16
444	5.11 ± 0.08		5.11

^aRefs. [16] and [17].

^bRef. [7].

The resulting transition energies are given in Table 4 and are compared with the results of Kleinman and Phillips who employed the same exchange modifications. Although the latter results were obtained by a self-consistent calculation in which the Brillouin zone was sampled to correct the potential coefficients, this could not overcome the errors introduced by unimproved core functions and an overestimated average potential (-3.0 Ry vs. -1.88 Ry in the present calculations). There is also a comparison in the Table with the self-consistent OPW calculation of Herman *et al.*[4], in which an unmodified ' $\rho^{1/3}$ exchange' was employed.

ture experimentally determined indirect gap ($\Delta_1^{\text{min}} - \Gamma_{25}'$) as one constraint. This constraint fixes the insensitive transitions such as $\Gamma_{15} - \Gamma_{25}'$ at the same time, but there is still some latitude in determining sensitive levels such as $L_1(2)$ and Γ_2' . $L_1(2)$ is the most important of these levels, but, unfortunately, a transition energy involving this state has not been determined with sufficient accuracy. Herman *et al.* have, therefore, used three different values for the $L_1(2) - L_3'$ transition as the second constraint on their adjustments. (Subsequently, Herman[5] resolved a 'best estimate' for $L_1(2) - L_3'$ from a three parameter adjustment scheme.) The two parameter

Table 4. Comparison of theoretical transition energies (eV)

Transition	With Brooks correction		<i>k</i> -dependent exchange		
	Kleinman and Phillips ^a	Present results	Kleinman and Phillips ^a	Present results	Herman <i>et al.</i>
$\Gamma_{25}' - \Gamma_1$	10.28	10.98	20.26	17.40	
$\Gamma_{15} - \Gamma_{25}'$	2.88	3.28	2.48	2.95	3.05
$\Gamma_2' - \Gamma_{25}'$	8.55	3.42	8.68	3.52	2.8
$X_1(2) - \Gamma_{25}'$	2.40	2.22	1.62	1.58	1.65
$L_1(2) - \Gamma_{25}'$	5.11	2.42	4.95	2.17	1.8
$X_1(2) - X_4$	5.24	4.76	4.69	4.30	4.2
$L_1(2) - L_3'$	7.03	3.57	6.74	3.38	2.9
$L_3 - L_3'$	5.68	5.75	4.94	5.39	5.3

^aRef. [7].

^bRef. [4].

4. PERTURBED OPW CALCULATION

Herman *et al.*[4] have used an empiric perturbation scheme to bring their theoretical energy level spectrum into agreement with experiment. After determining the sensitivities of various levels to changes in leading potential coefficients v_H , they obtained values to which the coefficients must be altered to give the desired results. These changes, Δv_H , are considered as Fourier components of a crystal potential perturbation, ΔV , having both local and non-local components.

Their two parameter adjustment scheme for silicon required changes of approximately 3 per cent to v_3 and v_8 using the room tempera-

result with 'best $L_1(2) - L_3'$ value' is included in Table 5 along with experimental values and our present perturbation calculation.

In examining the sensitivities of the various energy levels to small changes in the leading Fourier coefficients of potential, we find that for small changes in v_3 , the Γ_{25}' level is ten times as sensitive as is Δ_1^{min} , the conduction band minimum, while the $L_1(2)$ and L_3' sensitivities are approximately equal. For small changes in v_8 , however, the $\Delta_1^{\text{min}} - \Gamma_{25}'$ transition is not affected, while the $L_1(2)$ is almost ten times as sensitive as the L_3' level. In addition, Δv_8 causes L levels to shift in opposite directions. Since our results in Table 4 agree

Table 5. Comparison of experimental transition energies (in eV) with those calculated by perturbed OPW methods

Transition	Experiment	Herman <i>et al.</i> ^a	Present results
$\Gamma'_{25} - \Gamma'_1$	17.0 ^e		17.5
$\Gamma'_{15} - \Gamma'_{25}$	2.85 ^f	2.7	2.86
$\Gamma'_{15} - \Gamma'_{25}$		4.2	3.54
$X'_1(2) - \Gamma'_{25}$		1.3	1.35
$\Delta'_1(2) - \Gamma'_{25}$	1.13 ^g	1.13	1.18
$L'_1(2) - \Gamma'_{25}$		2.25	2.06
$X'_1(2) - X'_1$	4.1-4.25 ^{f,h,j}	4.1	4.13
$L'_1(2) - L'_1$	3.0-3.4 ^h	3.4	3.29
$L'_3 - L'_1$	5.3 ⁱ	4.95	5.27
$\Delta'_1(2) - \Delta'_3$	3.2-3.4 ^{h,k}	3.5	3.22
$\Delta'_1(2) - \Delta'_5$		3.4	3.42
$\Sigma'_3(2) - \Sigma'_2$	4.3-4.4 ^{h,j,k}	4.3	4.33
$W'_1(2) - W'_2$			8.46

^aA transition at $2\pi/a$ (0.25, 0.25, 0.25).

^b Δ transition at $2\pi/a$ (0.5, 0.0).

^c Σ transition at $2\pi/a$ (0.5, 0.5, 0).

^dRefs. [4] and [5].

^eRef. [18].

^fRef. [19].

^gRoom temperature value. Gap is 1.15 eV at 90°K — Ref. [20].

^hRef. [4].

ⁱRef. [21].

^jRef. [22].

^kSee deformation potential discussion in Section 6.

with experimental estimates, in spite of the sensitivity of many transitions to slight changes of v_3 and v_8 , our core functions and the exchange modifications may be indicative of a reasonable description of the silicon lattice. In contrast, the majority of the transitions are unaffected by changes of 0.1 Ry in v_0 .

Some of our differences between theoretical and experimental transition energies may be due to our use of a spherically symmetric valence potential which is not corrected by a sampling of the Brillouin zone for the core states determination. Quelle[9] found that these corrections were of the order of 0.02 Ry for v_3 and 0.00012 Ry for v_8 , whereas Kleinman and Phillips[7] have indicated that their corrections were much larger using the sampling scheme: the corrections may be in error by as much as 0.03 Ry for v_3 and 0.003

Ry for v_8 due to the relatively small number of Brillouin zone points sampled.

In order to correct for a non-spherically symmetric valence charge distribution, we use atomic scattering factors, $f(\vec{H})$, rather than zone sampling as a basis for adjustment. The agreement between theoretical and experimental scattering factors for higher $\vec{H}$ values in Table 3 indicates that the spherically symmetric valence potential employed is responsible for some of the disagreement at lower $\vec{H}$ values, since deviations from spherical symmetry affect $f(111)$ most significantly and also contribute to $f(220)$. Our adjustment consists of changes in the (111) and (220) electronic Coulomb potential coefficients that shift the values of associated atomic scattering factors into agreement with the experimental values in Table 3. Therefore, an adjustment of 0.0095

Ry is applied to the (111) valence Coulomb coefficient, while the (220) component is altered by 0.0026 Ry. Both perturbations are smaller than the corresponding changes of Herman *et al.* and are in the range of the corrections obtained in sampling the Brillouin zone to obtain a self-consistent valence potential. Using these adjusted coefficients we obtain the improved values of the transition energies listed in Table 5.

The results of Herman *et al.* were adjusted to the room temperature indirect gap, while our corresponding 1.18 eV transition is more consistent with the value for stationary atoms for which the OPW method is formulated. Additional discussion on the interpretation of experimental data for silicon is given in Dresselhaus and Dresselhaus[23]. The electronic energy band structure is shown in Figs. 1 and 2 in accordance with the present results in Table 5. No interpolation procedure is used to obtain these plots, since calculations are performed at many general points as well as

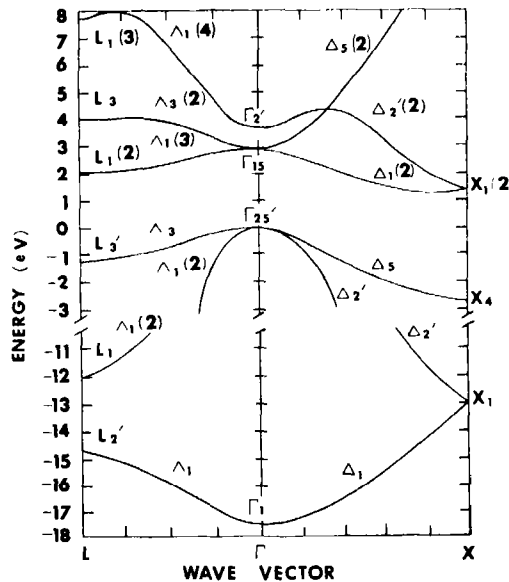


Fig. 1. Theoretical electronic energy band structure of silicon along Δ and Λ axes. (Energy scale is based on $E(\Gamma_{25}') = 0$.)

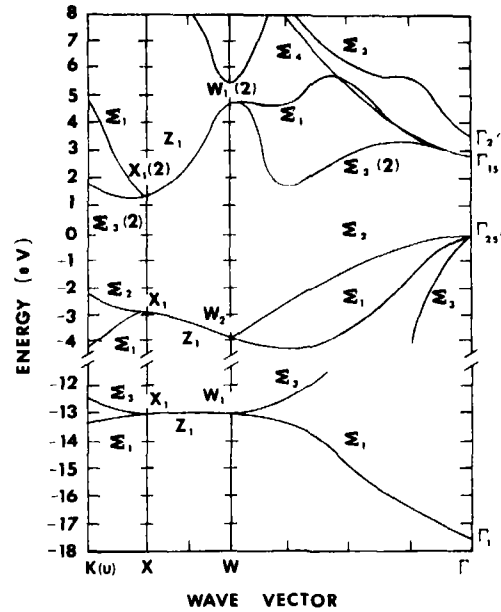


Fig. 2. Theoretical electronic energy band structure of silicon along Σ' , Z , and Σ axes. (Energy scale based on $E(\Gamma_{25}') = 0$.)

those of high symmetry. A more detailed analysis of the band extrema is given in the next section.

5. EFFECTIVE MASSES

In our OPW calculation, precise determination of the conduction band longitudinal effective mass m_l^* , at $(2\pi/a)(k_m, 0, 0)$ is hindered by the difficulty in locating the minimum, k_m . Assuming a parabolic band with energy E_m at k_m , the energy E_x at $(2\pi/a) \times (k_x, 0, 0)$ along the parabola is

$$E_x = E_m + (\hbar^2/2m_l^*)(2\pi/a)^2|k_x - k_m|^2. \quad (13)$$

Using 112 OPW's the energies at points $0.80 \leq k_x \leq 0.85$ indicate k_m is between 0.820–0.825 and corresponds to $0.955m_0 \leq m_l^* \leq 0.905m_0$. This is to be compared with the experimental values of approximately $0.92m_0$ shown in Table 6. Herman *et al.*[4] determined $k_m = 0.81$, while an earlier, often used, experimental value [24] was 0.85 ± 0.03 .

Table 6. Comparison of theoretical and experimental effective mass parameters. (m^* in units of m_0)

Representation	Present calculation	Dresselhaus and Dresselhaus ^a	Experiment
$\Gamma'_{25}(\Gamma'_7)$	$m_h^* = -0.255$	-0.25	-0.25 ± 0.01^d
$\Gamma'_{25}(\Gamma'_8)$	$A = -3.921$	-3.90	$-4.22^a - 4.27 \pm 0.02^b$
	$B = 1.445$	1.03	$1.0^a \quad 0.63 \pm 0.08^b$
	$C = 4.35$	3.79	$4.34^a \quad 4.93 \pm 0.15^b$
Δ_1^{min}	$m_l^* = 0.93 \pm 0.025$	0.98	0.9163 ± 0.0004^f
	$m_l^* = 0.215$	0.20	0.1905 ± 0.0001^f
L'_1	$m_l^* = 1.66$	1.53	
$L_1(2)$	$m_l^* = 2.11$	1.32	
L_1	$m_l^* = 6.3$	-1.45	

^aRef. [27].

^bRef. [28] as corrected by Ref. [29].

^cRef. [26].

^dRef. [25].

^eRef. [23].

^fRef. [30].

Figure 3 shows the energy bands perpendicular to the Γ - X axis close to the wave vector of the conduction band minimum. These energies are calculated using approximately 112 OPW's per point for the (011) and (010) directions parallel to the K - X and X - W axes,

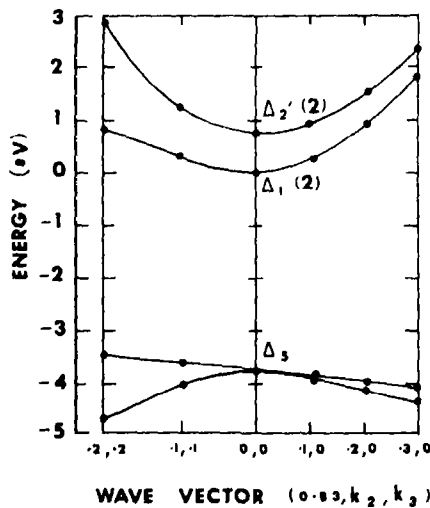


Fig. 3. Theoretical electronic energy band structure of silicon in directions perpendicular to the Δ axis at the conduction band minimum. (Energy scale is based on $E(\Delta_1(2)) = 0$.) Wave vector components in units of $2\pi/a$.

respectively. The curvature of the $\Delta_1(2)$ derived band in the (010) direction corresponds to an electron effective mass of $0.215m_0$ and is in reasonable agreement with average values of the transverse effective mass determined experimentally, as shown in Table 6.

For determination of the hole effective masses we calculate the energies for several points about the valence band maximum, Γ'_{25} , along the Δ and Λ axes. Γ'_{25} is triply degenerate (aside from spin degeneracy) and splits into a doubly degenerate Γ'_8 and non-degenerate Γ'_7 under spin-orbit interaction [25]. In the X and L directions, respectively, Γ'_8 becomes the Δ_7 and Λ_6 heavy hole band and the Δ_8 and $\Lambda_4 + \Lambda_5$ light hole band, while Γ'_7 becomes the Δ_7 and Δ_6 split-off band. The curvatures of the $\Gamma'_8 - \Delta_7$ and $\Gamma'_8 - \Delta_6$ bands are obtained from $\vec{k} \cdot \vec{p}$ perturbation theory [28] as

$$E^\pm(k) = E(0) + (\hbar^2/2m_0) \times \{Ak^2 \pm [B^2k^4 + C^2(k_x^2k_y^2 + k_y^2k_z^2 + k_x^2k_z^2)]^{1/2}\}, \quad (14)$$

while the split-off band is

$$E(k) = E(0) + (\hbar^2/2m_0)Ak^2 - \text{spin-orbit splitting}. \quad (15)$$

In order to calculate the coefficients A , B and C , determined from cyclotron resonance experiments, we assume that since the spin-orbit splitting in silicon is so small (approximately $0.0032 R_y$), the band curvatures are not changed appreciably by the splitting. That is, the bands $\Gamma_8^+ - \Delta_7$, $\Gamma_7^+ - \Delta_7$, $\Gamma_8^+ - \Lambda_6$, and $\Gamma_7^+ - \Lambda_6$ have the same curvatures as $\Gamma_{25}' - \Delta_5$, $\Gamma_{25}' - \Delta_2$, $\Gamma_{25}' - \Lambda_3$, and $\Gamma_{25}' - \Lambda_1$ respectively. Using approximately 116 OPW's per point and equations (14) and (15) results in valence band mass parameters in agreement with experimental values.

In Table 6, we include the calculated effective masses for some bands in the (111) direction at L . There is not, at present, experimental data for these parameters, so that we can compare them only with those masses obtained by Dresselhaus and Dresselhaus[23] from their Fourier expansion method based on experimentally determined transition energies and mass parameters. (They used an $m_i^* = 0.97 \pm 0.02 m_0$ for the conduction band at Δ^{min} rather than the more recent values of approximately $0.92 m_0$). There does not appear to be any general agreement.

6. DEFORMATION POTENTIALS

By recomputing the electronic energy bands for different lattice constants, the deformation potentials[31], D , may be obtained in order to identify the levels associated with pressure dependent transitions. Herman *et al.*[4] calculated the silicon band structure for 0.90 – 1.1 times the lattice constant, $a_0 = 10.2632 B.U.$, and then employed three- and five-point interpolation to obtain the D values, changes in energy per unit dilatation. These results were based on their OPW results and not on the perturbation scheme which improved these results.

We recalculate the band structure at $0.95 a_0$ only, since this lattice constant represents an upper limit on pure hydrostatic pressure used successfully on silicon crystals[32] (approximately $140,000 \text{ kg/cm}^2$), and the pressure dependence of the indirect gap was found to

be linear up to this pressure (although the compressibility is nonlinear in this region) [33]. In recalculating the potential coefficients with the smaller lattice constant, X-ray data is unavailable for adjustment of the (111) and (220) valence Coulomb coefficients. The adjustment employed is to change these coefficients by the same percentages used in the original calculation. Whereas Herman *et al.* have calculated the deformation potential for the $\Gamma_{25}' - X_1(2)$ transition and assigned the same value to the $\Gamma_{25}' - \Delta_1^{min}$ transition, our results show the $\Gamma_{25}' - \Delta_1^{min}$ D value is smaller than that of the $\Gamma_{25}' - X_1(2)$ transition. It appears that the position of Δ_1^{min} is not changed significantly by the smaller lattice constant, although the longitudinal effective mass increased from approximately $0.93 m_0$ to $1.03 m_0$. This is equivalent to

$$1/m_i^* |(\partial m_i^*/\partial p)_T| = 0.75 \text{ per unit dilatation}$$

which is approximately $0.74 \times 10^{-6} \text{ cm}^2/\text{kg}$. A calculation by Nathan[34] produced a pressure dependence of $5 \times 10^{-6} \text{ cm}^2/\text{kg}$ for an average effective mass.

The theoretical transition energies for the reduced lattice constant are listed in Table 7 along with corresponding D values which are compared with previous calculations and experiments. Our deformation potential results are in agreement with those of Herman *et al.* and have the correct pressure dependence of the indirect gap. Referring to Table 5 and Figs. 1 and 2, it appears that the 4.4 eV peak is associated with the $\Sigma_3(2) - \Sigma_2$ transition along the (110) axes, while the 3.38 eV peak may be due to transitions in the extended region of the reduced zone beyond point L . Herman *et al.* have reached essentially the same conclusions from their results.

7. SUMMARY

Our results suggest that the correlation and exchange approximations, modified slightly, of Brooks[6] and Kleinman and Phillips[7] are applicable to the silicon band structure, and

Table 7. Theoretical transition energies in silicon at a lattice constant of 9.75 B.U. and comparison of theoretical and experimental deformation potentials, D . (D in eV per unit dilatation)

Transition	Present results energy (eV)	D	Herman <i>et al.</i> ^a D	Goroff and Kleinman ^b D	Experiment ^c D
$\Gamma'_{25} - \Gamma'_1$	18.59	7.6			
$\Gamma'_{15} - \Gamma'_{25}$	2.98	-0.85	-0.6	1.35	
$\Gamma'_2 - \Gamma'_{25}$	5.17	-11.8	-11.9	-8.6	
$X_1(2) - \Gamma'_{25}$	1.15	+1.42	+1.4	+0.3	
$\Delta_1^{\text{min}} - \Gamma'_{25}$	0.99 ^e	+1.32 ^e	+1.4 ^d		+1.5
$L_1(2) - \Gamma'_{25}$	2.72	-4.57	-4.1	-4.1	
$X_1(2) - X_4$	4.39	-1.79	-1.4	-2.3	
$L_1(2) - L_3$	4.12	-5.80	-5.2	-4.5	
$L_3 - L'_1$	5.50	-1.58	-1.1		
$\Delta_1(2) - \Delta_5^f$	3.67	-1.75	-1.3		
$\Sigma_3(2) - \Sigma_2^g$	4.72	-2.84	-3.1		
4.4 eV peak					-2.9 ± 0.5
3.38 eV peak					-5.2 ± 0.5

^aRef. [4].

^bRef. [35].

^cRef. [36].

^dUsed same value as for $X_1(2) - \Gamma'_{25}$.

^eCalculated for $\vec{k} = 2\pi/a$ (0.83, 0, 0).

^f Δ transition at $2\pi/a$ (0.5, 0, 0).

^g Σ transition at $2\pi/a$ (0.5, 0.5, 0).

that the results of a previous calculation, using these approximations, were adversely affected by incorrect core functions and an over estimate of the average potential. The procedure for obtaining core functions has proven successful as measured by the theoretical atomic scattering factors and energy band structure. The use of atomic scattering factors in improving the crystal potential has reduced the amount of work required to obtain an improved band structure by the OPW method. This procedure, however, may not be applicable when theoretical scattering factors differ significantly from experimental values. The reason for this is that only the Coulomb contribution to the potential is corrected by this method, and the exchange contribution will be incorrect if very large perturbations are required.

REFERENCES

- HERMAN F., *Phys. Rev.* **93**, 1214 (1954).
- WOODRUFF T. O., Thesis, Calif. Inst. of Tech. (1955); *Solid State Physics* (Edited by F. Seitz and D. Turnbull), Vol. 4, p. 367. Academic Press, New York (1957).
- HERRING C., *Phys. Rev.* **57**, 1169 (1940).
- HERMAN F., KORTUM R. L., KUGLIN C. D. and SHORT R. A., *Quantum Theory of Atoms, Molecules and Solids* (Edited by P. O. Löwdin), p. 381. Academic Press, New York (1966).
- HERMAN F., KORTUM R. L. and KUGLIN C. D., *Int. J. quant. Chem.* **18**, 533 (1967).
- KLEINMAN L. and PHILLIPS J. C., *Phys. Rev.* **116**, 880 (1959).
- KLEINMAN L. and PHILLIPS J. C., *Phys. Rev.* **118**, 1153 (1960).
- SLATER J. C., *Phys. Rev.* **81**, 385 (1951).
- QUELLE F. W., Jr., *Tech. Rep.* 295 Lincoln Lab. M.I.T. (17 Jan. 1963) unpublished.
- SLATER J. C., *Phys. Rev.* **36**, 57 (1930).
- SLATER J. C., *Phys. Rev.* **42**, 33 (1932).
- LÖWDIN P. O., *Phys. Rev.* **90**, 120 (1953).
- LÖWDIN P. O., *Phys. Rev.* **94**, 1600 (1954).
- HERMAN F. and SKILLMAN S., *Atomic Structure Calculations*. Prentice Hall, Englewood Cliffs, N.J. (1963).
- HEINE V., *Proc. R. Soc. Lond.* **240**, 361 (1957).
- DEMARCO J. J. and WEISS R. J., *Phys. Rev.* **137**, A1869 (1965).
- DAWSON B., *Proc. R. Soc. Lond.* **A298**, 379 and 402 (1967).
- SKINNER H. W. B., *Phil. Trans. R. Soc.* **A239**, 95 (1940).

19. MOORJANI K., To be published.
20. FROVA A. and HANDLER P., *Phys. Rev. Lett.* **14**, 178 (1965).
21. COHEN M. L. and PHILLIPS J. C., *Phys. Rev.* **139**, A912 (1965).
22. ALLEN F. G. and GOBELI G. W., *Phys. Rev.* **144**, 558 (1966).
23. DRESSELHAUS G. and DRESSELHAUS M. S., *Phys. Rev.* **160**, 649 (1967).
24. FEHER G., *Phys. Rev.* **114**, 1219 (1959).
25. ZWERDLING S., BUTTON K. J., LAX B. and ROTH L. M., *Phys. Rev. Lett.* **4**, 173 (1960).
26. DRESSELHAUS G., KIP A. F. and KITTEL C., *Phys. Rev.* **92**, 827 (1953); **95**, 568 (1954); **98**, 368 (1955).
27. STICKLER J. J., ZEIGER H. J. and HELLER G. S., *Phys. Rev.* **127**, 1077 (1962).
28. HENSEL J. C. and FEHER G., *Phys. Rev.* **129**, 1029 (1963).
29. BALSLEV I. and LAWAETZ P., *Phys. Rev. Lett.* **19**, 6 (1965).
30. HENSEL J. C., HASEGAWA H. and NAKAYAMA M., *Phys. Rev.* **138**, A225 (1965).
31. BARDEEN J. and SHOCKLEY W., *Phys. Rev.* **80**, 72 (1950).
32. SLYKHOUSE T. E. and DRICKAMER H. G., *J. Phys. Chem. Solids* **7**, 210 (1958).
33. PAUL W. and BROOKS H., *Progress in Semiconductors* (Edited by A. F. Gibson and R. E. Burgess), Vol. 7, p. 135. Heywood, London (1963).
34. PAUL W. and WARSCHAUER D. M., *Solids Under Pressure*, p. 178, Table 8-5. McGraw-Hill, New York (1963).
35. GOROFF I. and KLEINMAN L., *Phys. Rev.* **132**, 1080 (1963).
36. ZALLEN R. and PAUL W., *Phys. Rev.* **155**, 703 (1967).

COMPRESSIBILITY OF 18 METALS TO 45 kbar*

S. N. VAIDYA and G. C. KENNEDY

Institute of Geophysics and Planetary Physics, University of California, Los Angeles, Calif. 90024 U.S.A.

(Received 29 October 1969; In revised form 29 December 1969)

Abstract—Volume compressions of 18 metals and pyrophyllite, boron nitride and talc have been determined by monitoring piston displacements in an end-loaded piston-cylinder apparatus. The present values are at variance with Bridgman's piston-cylinder measurements in the same range; the discrepancy being greater for more compressible substances. Our values are in close agreement with Bridgman's hydrostatic lever-piezometer measurements up to 30 kbar on rod shaped specimens of Cu, Ag, Pb, Ta and Fe and also with the room temperature values derived from shock wave data using Dugdale-MacDonald equation for variation of $\gamma_0(V)$ along the 0°K isotherm. Intercomparison of isothermal bulk modulus, B_0 , and its pressure derivative, B'_0 , obtained from the static and the ultrasonic measurements at high pressures has also been made.

1. INTRODUCTION

BRIDGMAN's measurements of the compressibility of solids was almost our sole source of PVT data for solids for many years. During the last decade, however, the compressibility of numerous solids has been determined in high pressure X-ray cells and by shock wave methods. The elastic constants of solids determined in the low pressure region have also been used in accordance with different equations of states to obtain pressure-volume relationships to very high pressures. It is now of interest to intercompare the compressibility of solids as determined by these various methods. Such an intercomparison would, hopefully, not only bring out the limitation of each method but would test the validity of the various equation of state formulations used in converting dynamic data into isothermal compressibility data.

Unfortunately, much of the static compressibility data as reported by Bridgman is not sufficiently accurate for the purposes of an intercomparison. Bridgman repeated his measurements in a variety of apparatus configurations with results which for some substances were remarkably discordant, the

discordance being larger for the more compressible substances. Thus, in view of the uncertainty in his published results, it seems desirable to redetermine the compressibility of a number of elements, with the maximum precision available today, and to intercompare these static results from dynamic measurements.

Two different static methods of determining compressibility are available. One is by the use of high pressure X-ray cells and the other by making measurements of displacement at high pressures. High pressure X-ray cells are essentially of two designs. Piston cylinder geometry is used in one type of cell which has a pressure range up to about 25 kbars. The sample is encased in a beryllium cylinder and slots are made around the pressure vessel to admit X-ray beams. The effects of friction in this geometry are roughly the same as in an end loaded piston cylinder device and there seems to be no reason why unit cell volumes cannot be measured with $M\alpha K_\alpha$ radiation to a precision of approximately one part in 300. Anvils are normally used for pressures above 25 kbars and a sample is X-rayed between the anvils. The uncertainties in this kind of determination are as much as several percent of the cell edge, it is exceedingly difficult to estimate pressure, and X-ray signals are weak.

*Publication No. 779 Institute of Geophysics and Planetary Physics, University of California, Los Angeles, Calif. 90024, U.S.A.

Further, it is difficult to show that the sample under study is at the same pressure as the pressure transmitting medium between the anvils. Our limited experience with this kind of apparatus suggested extremely poor precision. As a result, we examined methods of determining compressibility by observation of piston displacement in piston cylinder apparatus. It was immediately clear that measurements of compression in this kind of apparatus could be made with a precision three-to ten-fold greater than was possible by X-ray methods available to us.

2. APPARATUS

Our apparatus for compressibility measurements is shown schematically in Fig. 1; the details of the sample arrangement are shown

in Fig. 2. The piston of carboloy, with 3 per cent cobalt bonder is from 0.4998 to 0.5000 in. dia. and 1.5 in. long. The clearance between the pressure vessel and piston did not exceed 0.0005 in. These pistons, fitted with Vascomax binding rings on the exposed end, in order to keep the length-diameter ratio of the piston small, served well to 45 kbar and undoubtedly we could have gone to substantially higher pressures. However, a pressure limit of 45 kbar was set to avoid permanent deformation of the tungsten carbide pressure vessel. The piston rests on a tungsten carbide cylinder of 1 in. dia. and 1 in. length. The piston was advanced by a 250 ton, 6 in. dia. hydraulic ram, *M*, operated by a hand pump. The oil pressure in the ram was read on a newly calibrated 14 in. face Heise Bourdon

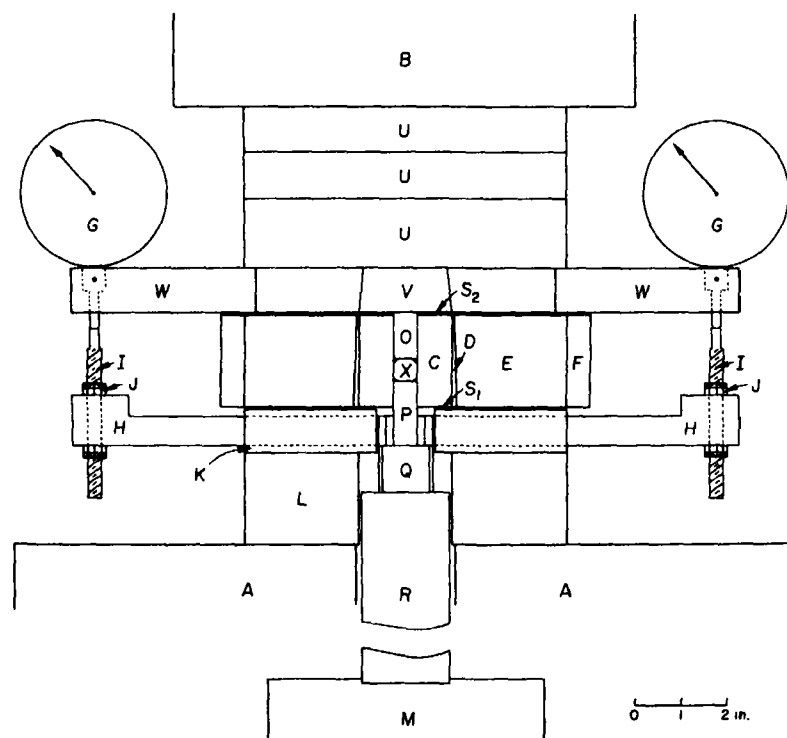


Fig. 1. Schematic diagram of the experimental arrangement for volume compression measurements.

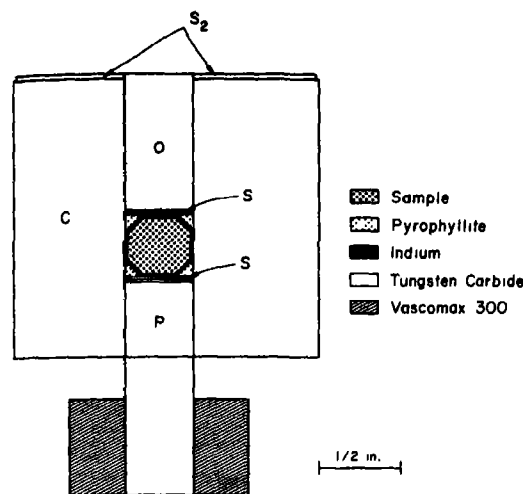


Fig. 2. Sample assembly.

tube gauge with gradations to 0.5 bar which corresponded to 72 bars pressure on the face of the $\frac{1}{2}$ in. dia. piston.

The pressure vessel, C, was of tungsten carbide, grade 883, with 6 per cent cobalt binder, of $\frac{1}{2}$ in. dia. and 2 in. o. d. It was surrounded by a tapered sleeve and forced into a Vascomax steel supporting ring, hardened to Rockwell 52. The tungsten carbide core pushed in with approximately 0.060 in. interference. This force was sufficient to shrink the bore of the pressure chamber by approximately 0.005 in. The moveable end load platen A applies a compressive force to the ends of the carbide pressure vessel through a shim, S₁. This force was maintained at approximately 250 tons and was sufficient to prevent horizontal fractures in the tungsten carbide pressure vessel. The sample was retained in the center of the pressure vessel by a fixed tungsten carbide element, O, which abutted against a large tapered tungsten carbide cylinder, V.

The compressibility of the sample was determined by measuring the change in distance between the two lever arms H and W as the pressure was raised. This distance was

measured by two Ames dial gauges, model 316-5, the smallest gradation 0.0001 in. Unfortunately, because of the lack of exact parallelism of all the mating service, the two gauges did not record the same displacement as the piston was advanced. The maximum distance and the values of displacement as reported by the two gauges never disagreed by more than 0.01 in. The difference tended to diminish with more highly compressible substances. The average of the displacement, as read on the two gauges, in various runs on a given substance was reproducible to 0.0001 in. However, it was found essential to take a mean of the two readings in order to obtain reproducible results.

It is self evident that to obtain high accuracy in measurements of compressibility the contribution of the sample to the volume change should be optimized and the apparatus constants should be reproducible. In our apparatus, the contribution of chamber deformation and compressions of the piston P and plug O to the observed displacement are small and highly reproducible.

It is interesting to compare the contribution of the volume change of the sample to the total observed piston displacement in our apparatus and in Bridgman's 1940 apparatus which operated to the same pressure limit. Bridgman's apparatus employed an alloy steel pressure chamber and carboloy pistons of 0.25 in. dia. and 0.25 in. long. He found, that with a sample of iron sheathed in indium in the pressure chamber, the total displacement at 50,000 atm was 0.065 in., of which 0.016 in. was contributed by distortion of the press, 0.011 in. by actual compression of the iron, 0.022 in. by compression of the indium, and 0.016 in. by dilation of the pressure vessel[1]. Thus, somewhat less than 25 per cent of the total displacement was owing to compression of a sample and the corrections to the raw data amounted to 75 per cent of the observation. In our experiment at 45 kbar, the piston displacement on an iron sample was 0.039 in., of which 0.020 in. was owing to apparatus constants

and 0.019 in. was owing to compression of iron. Thus, our relative corrections were lower than Bridgman's by a factor of almost 2 in the case of iron.

The length of the sample used was determined by the result of a compromise between the requirements that the pressure be hydrostatic and the requirement that the contribution of the volume change of the sample to the total piston displacement be relatively large. Pressure tends to become more and more hydrostatic as the length of the sample is diminished, however, the contribution of compression of sample to total piston displacement directly varies with sample length. Throughout our experiments we used samples with an initial length of approximately 0.5 in.

The details of the sample assembly are shown in Fig. 2. The cylindrical sample was completely surrounded by an indium sheath 0.006 in. thick. Pyrophyllite mitre rings of 0.065 in. prevented extrusion of the indium and sample along the walls between the piston and the vessel. A steel shim separated the indium from the face of the pistons *P* and *O*. Indium tends to penetrate minute cracks and we found that the presence of steel greatly enhanced the life of the pistons and their operation. The weight of the sample, the pyrophyllite mitre rings, the steel shims and the indium are all determined and enter into the corrections made in the final observation.

Each new pressure vessel was seasoned by filling it with lead and cycling it a number of times to the maximum pressure. This seasoning gave a maximum initial permanent dilation of the present chamber of approximately 0.0005 in. and in subsequent runs the diameter of the pressure vessel did not increase by more than 0.0002 in.

The elastic dilation of the pressure vessel at high pressures was determined from two experiments with varying amounts of tungsten carbide and lead in 0.5 in. long sample assemblies. Tungsten carbide was in the form of 0.375 in. dia. 0.065 in. thick slugs. The apparatus constant was estimated from a car-

boloy run, which consisted of replacing the 1.0 in. long carboloy plug, *O*, by a 1.5 in. long plug separated from piston *P* by two 0.001 in. thick pieces of lead foil. These three sets of runs gave the apparatus constant and yield the value Δ , the dilation of the cylinder.

The initial measurement of the apparatus constant was used only in determination of the cylinder dilation. In practice, every fourth or fifth run was made on a sample of gold. These runs indicated that the apparatus constant did not change with time. However, all our results, as presented later, are referred to the compressibility of gold.

The measurements

The piston displacement, as determined by averaging the readings of the two Ames dial gauges, was plotted as a function of pressure on both compression and decompression cycles. This gave a hysteresis loop in which the difference between the two readings at fixed displacement gave a measure of friction. One part of the friction arises from the friction between the piston, the high pressure seal and the internal surface of the pressure vessel and the remaining part of the friction comes from the failure of the sample to transmit pressure hydrostatically. This latter portion of the friction depends on the shear strength of the material and the inherent compressibility of the material. The data was plotted graphically and the mean taken. Displacements were read off our curves at 5 kbar intervals and used in the compressibility calculations.

Method of calculation of volume compression

The volume compression calculation essentially follows the method used by Bridgman [1]. It is briefly described here.

Let M_s , M_{py} , M_{in} be masses of the sample, pyrophyllite and indium respectively in the sample assembly, l_s^0 and l_s be the length of the assembly initially and at pressure *P*.

Let M_{au} , M'_{py} , M'_{in} be masses of gold, pyrophyllite and indium respectively in the

gold assembly, l_{au}^0 and l_{au} be the length of the assembly initially and at pressure P .

Let $v_s^0(v_s)$, $v_{au}^0(v_{au})$, $v_{py}^0(v_{py})$ and $v_{in}^0(v_{in})$ be volumes of 1 gm. of sample, gold, pyrophyllite and indium respectively initially (at pressure P).

Let Δl_s and Δl_{au} be the observed piston displacement of the sample and gold assemblies at pressure P .

Let s_0 and $s_0(l+\Delta)$ be the area of cross-section of pressure vessel initially and at pressure P .

We have then the following equations for two experiments.

$$M_s \cdot v_s^0 + M_{py} \cdot v_{py}^0 + M_{in} \cdot v_{in}^0 = s_0 \cdot l_s^0 \quad (1)$$

$$M_s \cdot v_s + M_{py} \cdot v_{py} + M_{in} \cdot v_{in} = s_0(l+\Delta) \cdot l_s \quad (2)$$

$$M_{au} \cdot v_{au}^0 + M_{py} \cdot v_{py}^0 + M_{in} \cdot v_{in}^0 = s_0 \cdot l_{au}^0 \quad (3)$$

$$M_{au} \cdot v_{au} + M_{py} \cdot v_{py} + M_{in} \cdot v_{in} = s_0(l+\Delta) l_{au} \quad (4)$$

Since the masses of various substances, their specific volumes and the area of cross section are known, equations (1) and (3) give l_s^0 and l_{au}^0 , the theoretical length of the assemblies. Subtracting (4) from (2) gives

$$1 + \Delta = \frac{v_{WC}(M'_{Pb} \cdot M_{WC} - M'_{Pb} \cdot M_{WC}) + v_{py}(M'_{Pb} \cdot M_{py} - M_{Pb} \cdot M'_{py})}{s_0(l_s M'_{Pb} - l'_s M_{Pb})} \quad (9)$$

$$M_s \cdot v_s = M_{au} \cdot v_{au} + (M'_{py} - M_{py})v_{py} + (M'_{in} - M_{in})v_{in} + s_0(l+\Delta)(l_s - l_{au}). \quad (5)$$

Since

$$l_s = l_s^0 - \Delta l_s + (\text{correction for press deformation}) \quad (6)$$

$$l_{au} = l_{au}^0 - \Delta l_{au} + (\text{correction for press deformation}) \quad (7)$$

and the correction for press deformation is taken to be the same for the two experiments performed under similar conditions, we get

$$l_s - l_{au} = (l_s^0 - l_{au}^0) - (\Delta l_s - \Delta l_{au}).$$

The final expression for the specific volume of sample v_s in terms of specific volumes v_{au} of gold becomes

$$\begin{aligned} M_s \cdot v_s &= M_{au} \cdot v_{au} + (M'_{py} - M_{py})v_{py} \\ &+ (M'_{in} - M_{in})v_{in} + s_0(l+\Delta) \\ &\times [(l_s^0 - l_{au}^0) - (\Delta l_s - \Delta l_{au})]. \quad (8) \end{aligned}$$

Calculation of Δ , cylinder dilation

Two runs with varying amounts of tungsten carbide (WC) and lead along with a blank run with WC are used for estimation of Δ . If M_{WC} , M_{Pb} and M'_{WC} and M'_{Pb} are the masses of tungsten carbide and lead in the two experiments and l_s and l'_s the length of the assemblies, then from two equation analogous to (1), l_s^0 and l'_s can be obtained. The equations analogous to (2) for these experiments are

$$\begin{aligned} M_{WC} \cdot v_{WC} + M_{py} \cdot v_{py} + M_{Pb} \cdot v_{Pb} &= s_0(l+\Delta) \cdot l_s \\ M'_{WC} \cdot v_{WC} + M'_{py} \cdot v_{py} + M'_{Pb} \cdot v_{Pb} &= s_0(l+\Delta) \cdot l'_s. \end{aligned}$$

Eliminating v_{Pb} from equations gives these

$$\text{where } l_s = l_s^0 - \Delta l_s + (\text{correction for press deformation}) \quad (10)$$

$$l'_s = l'_s{}^0 - \Delta l'_s + (\text{correction for press deformation}). \quad (11)$$

The correction for press deformation is estimated from a blank run with tungsten carbide. In this run 1.5 in. long plug, 0, is used instead of the 1.0 in. long plug in the conventional assemblies. Thus the displacements, other than those from the linear compression of 0.5 in. length of carbide, should be correction for press deformation. In

practice, best values were obtained assuming the compressive stress acting on O and P to be uniaxial. Thus the correction for press deformation in equations (10) and (11) equals

$$\left[1 - \frac{0.5 \text{ in.}}{(\text{length of } O + \text{length of } P) \text{ in.}} \right] \quad (12)$$

× (displacements in the blank run).

Using these values in equations (10) and (11) and $v_{w'}$ for carboloy grade 999 from Bridgman[2], Δ was calculated at intervals of 5 kbar. The variation of Δ with pressure was found to be *parabolic* and not *linear* as was assumed by Bridgman[1].

Calculation of Δ requires the compression data on pyrophyllite, v_{py} , and computation of v_s requires v_m as well. These quantities are evaluated by iteration as is described in the following section. The soundness of equation (12) for calculating the correction for press deformation is judged from the calculated values of the specific volumes of gold.

Results

Pyrophyllite. The pyrophyllite used in these runs was ash-grey material, from the same stock which was used for making the mitre-rings. Two runs were made one with and the other without indium. For the bare sample the calculation of v_{py} was made with equation (8) with $\Delta = 0$, and v_{au} values taken from Bridgman's experiments[2]. This value of v_{py} is used in calculation of Δ from equation (9). v_{py} recalculated from equation (8) with the calculated value of Δ from measurements on the sample sheathed in indium is given in Table 2 ((a)-(g)). These values are used in all subsequent calculations.

Gold. Gold in the form of an ingot 0.5 in. dia. by 0.5 in. in length of 99.999 per cent purity and free from any pores, obtained from Research Organic and Inorganic Chemicals Company (ROIC). v_{au} was calculated from equations (3), (4), (7) and (12) with $M'_{in} =$

0, i.e., for a run without the indium sheath around the sample

$$M_{au} \cdot v_{au} + M'_{py} v_{py} = s_0(l + \Delta)l_{au} \quad (4')$$

and

$$l_{au} = l_{au}^0 - \Delta l_{au} + (\text{correction for press deformation}) \quad (7')$$

with the first and third term on the right hand side of equation (7) defined by equations (3) and (12) respectively. The values obtained from these experiments are tabulated along with Bridgman's values[2].

Relative volumes from ultrasonic data were calculated from the Murnaghan equation

$$P = \frac{B_0}{B'_0} \cdot \left\{ \left(\frac{V_0}{V} \right)^{B'_0} - 1 \right\}. \quad (13)$$

Isothermal bulk modulus $B_0 = 1664$ kbar and its pressure derivative $B'_0 = 6.51$ calculated by Barsch and Chang[3] from the elastic constants measurements of Daniel and Smith[4] were used for the present calculations. In addition the values calculated for us from shock wave Hugoniot data by Keeler[5] are shown in Table 1. The data were taken from the compendium of shock wave data, University of California, Lawrence Radiation Laboratory.

Directly measured values of elastic constants are accurate to ± 0.5 per cent. The purpose in calculating the absolute compressions of gold here has been to check the equation (12) used in calculation of Δ . The absolute measurements has larger inaccuracies because of uncertain corrections for the apparatus deformation. The differential measurements are however more accurate because of cancellation of this term. In view of this, we have taken for all our calculations the volume compressions of gold determined from the ultrasonic measurements.

Silver. Our supply of silver in the form of 0.25 in. dia. rods was obtained from Research

Table 1. *Dilation of the pressure chamber, Δ , and volume compressions of gold*

P	$l + \Delta$	Gold $\rho = 19.302 \text{ g/cm}^3$			
		Present work	Ultrasonic data†	Bridgman	Shock
0	1.0000				
5	1.0007	0.9966	0.99703	0.99712	
10	1.0015	0.9932	0.99412	0.99430	
15	1.0026	0.9899	0.99128	0.99149	0.992
20	1.0040	0.9867	0.98850	0.98877	0.990
25	1.0056	0.9841	0.98577	0.98608	0.987
30	1.0077	0.9821	0.98310	0.98314	0.985
35	1.0100	0.9805	0.98048	0.98099	0.982
40	1.0125	0.9786	0.97791	0.97861	0.980
45	1.0153	0.9777	0.97540	0.97643	0.977

*Extrapolated values.

†(V/V_0) values of Gold tabulated in this column have been used in all the subsequent calculations.

Organic and Inorganic Chemicals Company (ROIC). It had a stated purity of 99.999 per cent. A cylinder of about 0.7 in. dia. was cast from this material in a graphite crucible, and a specimen machined from this slug was used for the compression measurements. As the sample was turned on the lathe, the material inside was found to be clear and shiny and free from blow holes. Bridgman's measurements on silver were made up to 30 kbar and in the present work, these are extended to 45 kbar. The present experiment gives a somewhat higher value of V/V_0 than those obtained by Bridgman and from shock data.

Aluminum. Aluminum in the form of a 0.5 in. dia. cylinder of 99.999 per cent purity was purchased from ROIC. Measurements were also made on aluminum alloy 6061 T6 in form of a rod of 0.7 in. dia. obtained from Alcoa. The composition of this material supplied by the manufacturer is: Si 0.4–0.8, Fe 0.7, Cu 0.15–0.40, Mn 0.15, Mg 0.8–1.2, Cr 0.15–0.35, Zn 0.25, Ti 0.15 per cent and remainder aluminum. The same material was employed in making sealing cups for the alkali metal experiments. The measured relative volumes for this material are somewhat larger than those for pure aluminum. The volume compressions of pure aluminum from

the static and shockwave measurements are in fair agreement.

Barium. Barium metal in form of a large vacuum sealed redistilled ingot was obtained from the King Laboratories, Syracuse, N.Y. In an earlier work on Ba I–II transition pressure the barium metal from the same source was employed and the results of its detailed chemical analysis have been given [6]. The ingot was slightly dark grey on the outside; the stated purity of the metal was about 99.5 per cent. Specimens for the compression work were machined on a lathe under mineral oil to minimize oxidation. The sample was surrounded by indium foil and quickly transferred to the pressure chamber. At 45 kbar the V/V_0 values from the present work and Bridgman's experiments are 0.7195 and 0.725 respectively. At higher pressures we find this material to be more compressible than is reported by Bridgman. Since the present work extends only to 45 kbar, the Ba I–II transition was not encountered.

Bismuth. Two compression measurements were made with bismuth of 99.999 per cent purity obtained from A. D. Mackay. Our samples came from the same stock of bismuth metal as the one earlier employed in the determination of the pressure of Bi III–V

transition[7]. The samples of proper dimensions prepared in a pill-press and were surrounded by indium foil. The volume compression from the two measurements are in close agreement and the pressures of Bi I-II and II-III transitions which could be easily resolved, were found to be the same for both the runs within the precision of the pressure measurements. The averaged values from the polynomial fit of the data of the two experiments are given in Table 1. Bridgman reported the transitions at 25.4 and 27.0 kbar respectively with the ΔV of the two transitions 0.086. We find the ΔV of Bi I-Bi II to be 0.0476 and the ΔV of Bi II-III to be 0.0339, a total for the two transitions of 0.0815, which compares well with Bridgman's value of 0.086. The pressures of Bi I-II and Bi II-III transitions determined in the present apparatus are 25.33 and 26.77 kbar respectively which are in good agreement with the values 25.38 and 26.965 kbar obtained by Kennedy and LaMori [8] in the rotating piston apparatus.

Calcium. Calcium used in this work was from an old laboratory stock of 1.5 in. dia., 6 in. long cylinders stored under mineral oil and of 99.5 per cent stated purity. Specimens machined from this stock under mineral oil showed very shiny and lustrous material inside. There were also no apparent blow

holes or flaws in the material. Two runs were made, one with indium foil surrounding the specimen and the other without it. Our compression values are in close agreement with shock data. Bridgman's V/V_0 values appear to be too low. At 45 kbar the V/V_0 values from this work is 0.8279, and 0.830 from Keeler's reduction from the shock wave data, whereas the value reported by Bridgman is 0.815.

Cadmium. Two experiments were made with cadmium metal. One sample was in the form of a cylinder 0.5 in. dia. and 99.99 per cent stated purity, obtained from ROIC. The second sample is about 0.65 in. dia. and was obtained by casting cadmium metal of 99.999 per cent stated purity from ARSCO in a graphite crucible. Specimens machined from these cylinders, encapsulated in indium foil were used in the present experiments. The measured values of V/V_0 from the two experiments were in close agreement and the average values are presented in Table 2 ((a)-(g)). The V/V_0 from the present work are only slightly lower than the shock values but are much larger than those reported by Bridgman. At 45 kbar the V/V_0 value from the present work is 0.9279 and those reported by Bridgman and from shock are 0.915 and 0.926 respectively.

Copper. Our sample of copper in the form

Table 2(a). Comparison of V/V_0 values from the present work with those of Bridgman and Keeler

Ag $\rho = 10.50 \text{ g/cm}^3$				Al $\rho = 2.70 \text{ g/cm}^3$			
<i>P</i>	Present work	Bridgman	Shock	<i>P</i>	Present work		Shock
					6061 T6	99.999%	
5	0.9955	0.995		5	0.9941	0.9937	0.993
10	0.9912	0.990		10	0.9885	0.9876	0.986
15	0.9870	0.986	0.987	15	0.9832	0.9817	0.980
20	0.9829	0.981	0.982	20	0.9782	0.9760	0.974
25	0.9789	0.977	0.978	25	0.9732	0.9704	0.969
30	0.9750	0.972	0.974	30	0.9683	0.9650	0.964
35	0.9712		0.970	35	0.9634	0.9597	0.960
40	0.9676		0.966	40	0.9584	0.9546	0.955
45	0.9641		0.963	45	0.9532	0.9497	0.951

* Refers to the density used in the present calculations.

Table 2(d)

P	In = 7.31 g/cm ³		La = 6.19 g/cm ³	
	Present work	Bridgman	Shock	Shock
5	0.9876	0.987	0.9805	0.980
10	0.9762	0.975	0.9624	0.963
15	0.9655	0.965	0.9456	0.947
20	0.9556	0.955	0.9300	0.931
25	0.9464	0.946	0.9155	0.915
30	0.9376	0.937	0.9019	0.903
35	0.9293	0.928	0.8890	0.890
40	0.9214	0.920	0.8768	0.880
45	0.9137	0.912	0.8651	0.870

Transition at 22.9 kbar with V/V_0 values 0.924 and 0.922.

Table 2(e)

P	Mo $\rho = 10.20 \text{ g/cm}^3$		Ni $\rho = 8.91 \text{ g/cm}^3$		Pb $\rho = 11.35 \text{ g/cm}^3$	
	Present work	Bridgman	Shock	Shock	Equation (14)	Shock
5	0.9980	0.997	0.9973	0.997	0.9885	0.988
10	0.9961	0.995	0.9947	0.994*	0.9777	0.977
15	0.9943	0.993	0.9923	0.991	0.9676	0.966
20	0.9925	0.991	0.9900	0.988	0.9581	0.957
25	0.9908	0.990	0.9878	0.986	0.9492	0.948
30	0.9892	0.989	0.9858	0.984	0.9411	0.940
35	0.9875		0.9839	0.982	0.9336	0.932
40	0.9860		0.9821	0.980	0.9267	0.924
45	0.9845		0.9805	0.978	0.9205	0.915

* Cusp at 10,500 kg/cm².

Table 2(f)

P	Sn = 7.30 g/cm ³			Ta = 16.70 g/cm ³			Ti = 11.85 g/cm ³	
	Present work	Bridgman	Shock	Present work	Bridgman	Shock	Present work	Bridgman
5	0.9911	0.991		0.9975	0.996		0.9870	0.987
10	0.9825	0.982	0.982	0.9951	0.994	0.995	0.9748	0.975
15	0.9742	0.973	0.974	0.9927	0.992	0.993	0.9633	0.965
20	0.9661	0.965	0.966	0.9903	0.990	0.990	0.9525	0.955
25	0.9584	0.958	0.959	0.9880	0.988	0.988	0.9425	0.946
30	0.9511	0.950	0.951	0.9857		0.985	0.9332	0.937
35	0.9440	0.942	0.944	0.9834		0.983	0.9247	0.929
40	0.9372	0.935	0.938	0.9811		0.981	0.9104*	0.911†
45	0.9307	0.928	0.931	0.9789		0.978	0.9030	0.903

*Ti II-III transition at 36.85 kbar with V/V_0 values 0.9220 and 0.9156.

†Ti II-III transition at 41.0 kbar with V/V_0 values 0.921 and 0.914.

Table 2(g)

P	Zn $\rho = 7.14 \text{ g/cm}^3$			pyrophyllite $\rho = 2.30 \text{ g/cm}^3$	Talc $\rho = 2.823 \text{ g/cm}^3$	BN $\rho = 2.20 \text{ g/cm}^3$
	Present work	Bridgman	Shock	Present work	Present work	Present work
5	0.9920	0.992		0.9849	0.9855	0.9761
10	0.9843	0.988		0.9741	0.9739	0.9596
15	0.9769	0.975		0.9658	0.9640	0.9462
20	0.9697	0.967	0.970	0.9598	0.9550	0.9344
25	0.9629	0.960	0.964	0.9540	0.9468	0.9240
30	0.9563	0.952	0.957	0.9489	0.9392	0.9135
35	0.9500	0.944	0.951	0.9437	0.9318	0.9036
40	0.9440	0.937	0.945	0.9388	0.9249	0.8940
45	0.9383	0.930	0.939	0.9339	0.9179	0.8848

of a cylinder of 99.999 per cent purity is owing to the courtesy of Mr. Howard Katzman of the Chemistry Department, UCLA. A cylinder of 0.65 in. was recast from this material in a graphite crucible and the measurements were made on a specimen machined from this cylinder. Our results indicate this material to be somewhat more incompressible than what is reported by Bridgman and from shock.

Iron. Two measurements were made of iron of 99.9 per cent stated purity obtained from ARMCO. The sample was in form of $\frac{1}{2}$ in. dia. bar stock and the machined specimens were surrounded by lead foil rather than our usual indium. The V/V_0 values from the present work are in close agreement with Bridgman's measurements up to 30,000 kg/cm². The present work extends the experimental data to 45 kbar. The V/V_0 values at 30 kbar from

this work and from Bridgman's measurements and shock are 0.9838, 0.986 and 0.983 respectively.

Indium. Indium metal in form of a 0.7 dia., 12 in. long rod was purchased from ROIC. It had a stated purity of 99.999 per cent. Indium metal from the same stock was also used for making the indium foil which was routinely wrapped around the specimens of other substances to reduce wall friction and to obtain a more hydrostatic distribution of pressure. There is excellent agreement between the values of V/V_0 from the present experiments and those computed from shock data; Bridgman's V/V_0 values are somewhat lower. At 45 kbar the V/V_0 from Bridgman's and the shock work are 0.912 and 0.915 respectively; the value from the present work is 0.9137.

Lanthanum. We owe the sample of lan-

thanum metal to the courtesy of Dr. Gary Dorer and Mr. Al Kerlin of the Department of Physics, UCLA. This material was in form of a cylinder 0.7 in. dia., 1.5 in. long obtained from Research Chemicals, Phoenix, Arizona. It had a stated purity of 99.9 per cent. The specimen for compression run was fabricated by machining under mineral oil to minimize oxidation. The V/V_0 values from our experiments are in close agreement with Bridgman's values up to 45 kbar. However, we did not observe the transition at 22.9 kbar with volumes 0.924 and 0.922 reported by Bridgman[9]. Indeed Bridgman also failed to observe this transition in lanthanum metal in his resistance experiments[10]. It seems therefore, possible that either this transition does not exist or it is too small to observe under the conditions of the present experimental set up.

Molybdenum. The specimen was machined from a rod 0.5 in. dia., 5 in. long, obtained from ROIC. It had a stated purity of 99.95 per cent. The volume compressions measured on this metal are in fair agreement with the values

this metal to be little less compressible than the estimates of Bridgman and from shock data.

Lead. Our supply of lead in form of a solid ingot was obtained from American Smelting and Refining Co. (ASRCO). It had a stated purity of 99.999 per cent. Two runs were made with cylindrical samples machined from the stock in different pressure vessels without indium foil around the samples. The volume compressions from the present measurements are in agreement with shock values. Bridgman reported compression at 45 kbar of 0.915, against 0.9204 obtained from the present work and 0.920 obtained from the shock wave data.

Rough compressions of lead can also be calculated from the experiments with samples consisting of lead and tungsten carbide inserts previously described for the calculation of chamber dilation Δ . With the notation introduced in that section, elimination of term V_{WC} , specific volumes of tungsten carbide leads to the equation for calculation of V_{pb} , i.e.

$$V_{pb} = \frac{(M'_{WC} \cdot l_s - M_{WC} \cdot l'_s) \cdot s_0 (1 + \Delta) - (M'_{WC} \cdot M_{py} - M_{WC} \cdot M'_{py}) V_{py}}{(M'_{WC} \cdot M_{pb} - M_{WC} \cdot M'_{pb})} \quad (14)$$

reported by Bridgman and the shock wave data. At 40 and 45 kbar we find this metal a little less compressible than indicated by the reduction of shock data.

Nickel. Our supply of nickel was in form of a cylinder 0.5 in. dia., 5.0 in. long, obtained from ROIC. It had a stated purity of 99.999 per cent. A specimen of 0.486 in. dia., 0.5 length machined from this stock was wrapped in indium foil. We observed a smooth volume-pressure relationship for this metal up to 45 kbar in contrast with Bridgman's observation of a cusp at 10,500 kg/cm² [2]. We believe that this discontinuity reported by Bridgman does not exist. At higher pressures the results from our experiment are in fair agreement with the values reported by Bridgman and from shock work. The V/V_0 values from this work indicate

The volume compressions evaluated from this equation are given along with the values obtained from the direct measurements. Agreement with the values from direct determinations and with shock values at 40 and 45 kbar probably indicates that the method of estimation of Δ becomes more and more precise at high pressures. This conclusion seems reasonable on consideration of the method used in the calculation of Δ .

Tin. Our supply of tin was obtained from ASRCO. It had a stated purity of 99.999 per cent. A rod of 0.60 in. dia. was cast from this material in a graphite crucible and the melt was cooled down slowly to avoid formation of any voids. The sample was machined from this slug and surrounded by a foil of indium. The specific volumes from our experiments

are slightly higher than these obtained by Bridgman; Keeler's values estimated from the shock wave data are in close agreement. At 45 kbar the V/V_0 values are 0.9307 from our experiments, 0.928 from Bridgman's work and 0.931 from the shock data.

Tantalum. We owe our samples to the courtesy of Dr. Gary Dorer, Department of Physics, UCLA. Tantalum was in the form of a polycrystalline rod of 0.5 in. dia. and had a stated purity of 99.99 per cent. Two experiments were made with specimens machined from this material and encapsulated in indium foil. The averaged values from the two experiments are given in Table 2 ((a)–(g)). The agreement with Bridgman's and the shock values up to 45 kbar is excellent.

Thallium. Cylinders of thallium metal from our old laboratory stock were used in the present experiments. The metal had been obtained some years ago from ASRCO and had a stated purity of 99.999 per cent. The material was dull grey on the outside and lustrous shiny metal appeared on scraping the external surface. The grey film was scraped from the sample and the specimens were prepared in a pill press. Two runs were made on the samples surrounded by indium foil. The Thallium II–III transition was sharp and the values of the transition pressures and the volumes V/V_0 from the two runs were in fair agreement. The averaged pressure of Tl II–III transition from the present work is 36.85 kbar with volumes before and after the transition of 0.922 and 0.9156. This may be compared with Bridgman's value of 41 kbar for the pressure of the Tl II–III transition and volumes 0.921 and 0.914, and 36.69 kbar for the transition obtained by Kennedy and La Mori[8] in a rotating piston apparatus. Agreement with Bridgman's and the shock values is fair up to 40 kbar.

Zinc. We owe this material to the courtesy of Mr. Howard of the UCLA Chemistry Department. It was stated to be 99.999 per cent pure. Two set ups were made and the values from the two experiments were in good

agreement. The present values are in a good agreement with estimates from the shock wave data. V/V_0 values reported by Bridgman are smaller; at 45 kbar Bridgman reported $V/V_0 = 0.930$ as against 0.9383 obtained from the present work and 0.939 computed from the shockwave data.

Talc and boron nitride. The volume compressions of talc and boron nitride are included in this paper along with those of pyrophyllite because of the frequent use of these substances in various high pressure assemblies. No measurements have been reported on these substances in the past. Talc specimen was machined from common laboratory stock obtained from American Lava Co. It is the same material as is used in making talc parts for other high pressure assemblies. Boron nitride was machined from 0.75 in. dia. cylindrical rod of binderless, hot pressed BN of 99.5 per cent purity obtained from Atlantic Equipment Engineers, Bergenfield, N.J. Both the specimens were surrounded by indium foil. At 45 kbar (V/V_0) values are 0.9179 for talc and 0.8848 for boron nitride. The volume compressions of these substances obviously are only approximate because of variation in porosity and composition from sample to sample.

3. DISCUSSION

The precision of our measurements is high. Duplicate measurements on relatively incompressible solids, such as Fe, Ta, Mo, etc. showed close agreement. At 45 kbar the range of V/V_0 was approximately 0.0005. However for the more compressible substances at the highest pressures, replicate measurements agreed only to 0.0015 in V/V_0 .

The accuracy of the measurements depends on the validity of the assumption of reproducibility of apparatus deformation, the estimation of the pressure vessel dilation at high pressure, Δ , and the corrections for friction in the apparatus. The reproducibility of apparatus deformation for the sample and gold runs

in a well seasoned pressure vessel is borne out by closely agreeing values on successive runs with gold and by the agreement in compression values calculated from two runs made on the same substance on different occasions. The estimation of pressure vessel dilation, Δ , also appears to be fairly good in view of the small divergence in the values of different pressure vessels made with the same interference and the same set of confining rings. The close agreement of the volume compressions of lead from the runs employed in calculation of Δ (equation (14)) with the values obtained from direct measurements gives further confidence in the present method of calculation of Δ .

The hysteresis in the piston-displacement pressure plot due to friction in the apparatus introduces the largest uncertainties in the calculation of volume compressions. The width of the hysteresis loop in a piston-cylinder apparatus depends on the sample material, the highest friction is encountered for metals with largest shear strength. Single value friction for the gold assembly at 40 kbar was typically 4.03 kbar which reduced to 3.32 kbar on surrounding the sample with indium foil. Representative values of single values of friction observed at 40 kbar for other substances surrounded by indium foil were: tantalum 4.46, nickel 4.3, lead 3.96, tin 3.02, cadmium 2.52, thallium 1.7, bismuth 1.5 and indium 1.44 kbar.

We have taken for purposes of comparison with the present work, Bridgman's volume compression from a recent review by Kennedy [11]. The values given in this review represent best fit of Bridgman's results published on various occasions and conversion of pressure units from kg/cm² to kbar is also made (Table 2(a)-(g)). The results are also expressed in the form of polynomial

$$\frac{\Delta V}{V_0} = aP + bP^2 + cP^3 \quad (15)$$

where P is in bar and the coefficients, a , b and

c were determined from the polynomial regression of the data. The corresponding values for Bridgman's data are taken from the review by Gschneider [12] who has taken into account the revised values on compression of iron, which was the standardizing substance used by Bridgman. Gschneider's values of the coefficients a , b , c are converted for P measured in bar. The results are given in Table 3.

The volume compressions determined from the present study are in general in good agreement with Bridgman's measurements in his 30,000 kg/cm² hydrostatic environment apparatus [2]. However, the overall agreement with his values measured in piston-cylinder apparatus is not so good. The agreement with Keeler's values calculated from shockwave Hugoniot is generally good. Bridgman's measurements on Ag, Cu, Fe, Mo, Ni and Ta up to 30,000 kg/cm² have been extended to 45 kbar in the present work. We find these metals in general less compressible i.e. the calculated V/V_0 values are higher than those obtained by Bridgman. The same trend is also observed in Ca, In, Pb and Zn for which we obtain larger V/V_0 values than those of Bridgman. On the other hand Ba and La are found to be slightly more compressible in the present work than suggested by Bridgman. In short, the overall agreement of the results of our experiments with shock wave values for most of the substances lends support to the method of calculation of isothermal compressions from the shock wave data.

Anderson [13] has derived the equation of a solid of the form

$$\frac{V}{V_0} = 1 - \left(\frac{P}{B_0}\right) + m\left(\frac{P}{B_0}\right)^2 - n\left(\frac{P}{B_0}\right)^3 + \dots \quad (16)$$

with $m = \frac{1}{2}(1 + B'_0)$, $n = \frac{1}{6}\{1 + 3B'_0 + 2(B'_0)^2 - B_0B''_0\}$ etc. where B_0 is the isothermal bulk modulus and B'_0 , B''_0 are its first and second order pressure derivatives.

Comparison of equations (15) and (16) gives relationships between the coefficients:

Table 3. Coefficients in the equation $\Delta V/V_0 = aP + bP^2 + cP^3$

Values in parantheses are the coefficients in polynomial fit to Bridgman's experimental data (Ref. (12))

Element	$-a \times 10^7$	$b \times 10^{12}$	$-c$	Range (kbar)	$\sigma \times 10^3$
Ag	9.031 (9.552)	2.3167 (0.317)		0-45 0-30	0.777 0.05
Al: 6061T6	12.281	8.793	1.0266×10^{-16}	0-45	0.121
Al	12.678 (13.327)	3.347 (4.678)		0-45 0-30	0.193 0.027
Ba	105.69 (93.359)	152.21 (88.861)	0.12415×10^{-14}	0-45 0-17	0.160
Bi (I)	32.286 (30.558)	26.529 (24.572)		0-25 0-20	1.35 0.244
Ca	54.757 (63.263)	54.206 (71.512)	0.39464×10^{-15}	0-45	0.753
Cd	21.140 (20.574)	11.358 (11.733)	0.434×10^{-15}	0-40 0-45	0.662 0.792
Cu	6.6211 (7.345)	1.0985 (2.00)		0-25 0-45	0.113 0.378
Fe	5.8441 (5.713)	1.5008 (0.7674)		0-30 0-45	0.008 0.362
In	25.709 (23.408)	20.143 (12.406)	1.2498×10^{-16}	0-45 0-50	0.227 0.101
La	40.623 (39.589)	31.874 (33.544)	0.18267×10^{-15}	0-45 0-23.4	0.702 0.186
Mo	3.951 (3.528)	1.1152 (0.125)		0-45 0-30	0.257 0.01
Ni	5.5475 (5.158)	2.7045 (0.519)		0-45 0-12	0.417
Pb	23.611 (22.379)	13.222 (8.962)			0.822 0.018
Sn	18.155 (17.750)	6.1227 (7.943)		0-45 0-30	0.229 0.046
Ta	4.9530 (4.795)	0.59394 (0.226)		0-45 0-30	0.322 0.006
Tl	26.646 (26.772)	14.623 (15.58)		0-35 0-25	1.03 0.079
Zn	16.271 (16.073)	5.6443 (7.285)		0-45 0-30	0.547 0.076

$$-a = \frac{1}{B_0},$$

$$b = m \cdot a^2 = \frac{1}{2B_0^2} \cdot (1 + B_0'), \quad (17)$$

$$-c = n \cdot a^3 = \frac{1}{6B_0^3} \cdot (1 + 3B_0' + 2(B_0')^2 - B_0B_0'').$$

Anderson's equation has found widespread interest because it enables one to derive the isothermal equation of static solids from the values of B_0 , B_0' , B_0'' obtained from the low

pressure elastic constant measurements. Owing to the presence of frictional effects in the piston-cylinder apparatus, the low pressure part of the P - V curve is not very precisely defined and are not very suitable for accurate determination of B_0 and B_0' . The isothermal bulk modulus and the derivatives are calculated from the adiabatic bulk modulus and its derivatives obtained from the ultrasonic wave velocity measurements. The results of these studies on Ag, Al, Cd, Cu, Fe and Pb are summarized in Table 4.

Table 4. Coefficients a and b calculated from volume compression measurements in piston-cylinder apparatus and the measurement of elastic constants at high pressure. The units of a and b are 10^{-7} bar^{-1} and $10^{-12} \text{ bar}^{-2}$ respectively

Element	Present work Polynomial fit		Present work Murnaghan equation		Bridgman data Gschneidner Polynomial fit		Ultrasonic measurements	
	a	b	a	b	a	b	a	b
Ag	9.03	2.31	8.27	1.192	9.55	0.317	9.85	3.17[4]
Al	12.67	3.34	12.83	4.433	13.33	4.678	13.22	5.405[14]
Cd	21.14	11.35	22.34	18.652	20.57	11.731	21.84	18.53*
Cu	6.62	1.09	6.15	0.27	7.34	2.0	7.50	1.73[4]
Fe	5.84	1.50	5.69	1.403	5.71	0.767	5.88	1.067[15]
							5.86	1.19[16]
							5.87	1.04[17]
							5.80	0.875[18]
Pb	23.62	13.31	25.01	24.27	22.38	8.96	23.87	19.14[19]

* Calculated from B_0 and m tabulated by Anderson[13] from the experimental values of J. A. Corl, ONR Report No. 6, June 1962, Case Institute of Technology.

In case of silver, aluminum and iron we find a fair agreement between the values of a and b obtained from the static and ultrasonic measurements. For cadmium and lead the values of b estimated from the Murnaghan equation fit and equation (17) are in better agreement with the ultrasonic work. The polynomial regression fit gives a lower value of b for these metals. We do not however understand the unusually small value of b for copper obtained from the Murnaghan equation.

Slater[20] has suggested that the Gruneisen parameter γ of a solid can be evaluated in terms of a and b as

$$\gamma = \frac{b}{a^2} - \frac{2}{3}.$$

Combining this with equation (17) gives

$$B'_0 = 2(\gamma + \frac{2}{3}) - 1. \quad (18)$$

However, the shock wave reduction by Dugdale-MacDonald formalism for these metals give indistinguishable results.

B_0 and B'_0 evaluated from the polynomial

regression and Murnaghan equation fit of the experimental data together with B'_0 calculated from equation (18) are summarized in Table 5. It may be observed that the compressibility parameter obtained from the polynomial regression and Murnaghan equation fit to the experimental data are somewhat different (Tables 4 and 5). This is not very surprising in the view of Anderson's detailed study of these two equation of states of the solids. Anderson has demonstrated by means of several examples that the Murnaghan equation gives a superior fit over the polynomials of all degrees. With the exception of Fe, Mo and Ni we find that generally B'_0 calculated from the static compression measurements and equation (18) are in a fair agreement. Gilvarry[27] has made such a comparison for some elements and found a poor agreement with Mo, Ta and Mn. Much of the disagreement noted by Gilvarry for Ta disappears with our revised measurements, though in case of Mo large discrepancy still exists. Although a good agreement had been previously noted for Fe and Ni with Bridgman's compression data[12], the present measurements on these metals show a large discrepancy.

Table 5. Compressibility parameters of the metals

Element	Polynomial fit		Murnaghan equation $2(\gamma + \frac{1}{2}) - 1$		
	B_0 (kbar)	B'_0	B_0 (kbar)	B'_0	$= B'_0^*$
Ag	1107.3	4.6810	1208.83	2.484	5.20
Al:6061T6	814.27	10.6600	875.85	3.214	
Al	788.77	3.1647	778.97	4.26	4.60
Ba	94.62	1.7252	94.32	2.187	2.02
Bi (I)	309.73	4.0901	296.93	6.742	2.42
Ca	182.63	2.6157	186.82	2.524	2.40
Cd	473.04	4.0830	447.6	7.307	4.88
Cu	1510.3	4.0115	1625.35	0.426	4.24
Fe	1711.1	7.7886	1757.56	7.669	3.72
In	388.97	5.0951	390.77	5.239	5.18
La	246.17	2.8630	244.73	3.150	1.64
Mo	2531.0	13.2879	2660.37	11.963	3.54
Ni	1802.6	16.5761	1904.8	20.157	3.98
Pb	423.53	3.7435	399.82	6.76	5.80
Sn	550.81	2.7152	549.20	3.651	4.76
Ta	2019.0	3.8421	2056.90	2.759	3.70
Tl (I)	375.29	3.1191	366.03	4.795	3.00
Zn	614.59	3.2639	597.91	4.880	4.38

*Values of γ taken from Gschneidner (Ref. (12)), p. 412.

ancy between the measured values of B'_0 and the ones calculated from equation (18).

Acknowledgements — Our grateful thanks are due to I. C. Gettling for many constructive suggestions and for writing the programs for IBM 360, for calculation of volume compressions, Murnaghan equation and polynomial regression fit of the data. Miss Sharon Bailey's assistance in processing of the experimental data and Mr. Geza Budai's assistance with the experimental work is deeply appreciated. Many thanks are owing to Richard Grover, Norris Keeler and Ed Royce of the Lawrence Radiation Laboratory for much help with the intercomparison of our results and the results from the shock wave experiments and many other constructive suggestions. We are also grateful to the S division of the Lawrence Radiation Laboratory for use of their very complete sonic data file. The excellent machining of the samples is due to Mr. J. Yamane and the upkeep of the apparatus is due to Mr. Les Faus. This research is supported by our AEC and I.R.L. contracts.

REFERENCES

- BRIDGMAN P. W., *Proc. Am. Acad. Arts Sci.* **74**, 21 (1940).
- BRIDGMAN P. W., *Proc. Am. Acad. Arts Sci.* **77**, 189 (1949).
- BARSCHE G. R. and CHANG Z. P., *Phys. Status Solidi*, **19**, 139 (1967).
- DANIEL W. B. and SMITH C. S., *Phys. Rev.* **111**, 713 (1958).
- KEELER R. N., *American Institute of Physics Handbook* (1970), (to be published).
- HAYGARTH J. C., GETTING I. C. and KENNEDY G. C., *J. appl. Phys.* **38**, 4557 (1967).
- HAYGARTH J. C., LUEDEMANN H. D., GETTING I. C. and KENNEDY G. C., *J. Phys. Chem. Solids* **30**, 1417 (1969).
- KENNEDY G. C. and I. A. MORI P. N., *J. geophys. Res.* **67**, 851 (1962).
- BRIDGMAN P. W., *Proc. Am. Acad. Arts Sci.* **76**, 71 (1948).
- BRIDGMAN P. W., *Proc. Am. Acad. Arts Sci.* **79**, 149 (1951).
- KENNEDY G. C., *American Institute of Physics Handbook* (1970), (to be published).
- GSCHNEIDNER K. A., JR., *Solid St. Phys.* **16**, 276 (1964).
- ANDERSON O. L., *J. Phys. Chem. Solids* **27**, 547 (1966).
- SCHMUNK R. E. and SMITH C. S., *J. Phys. Chem. Solids* **9**, 100 (1959).
- GUINAN M. W. and BESHAR D. N., *J. Phys. Chem. Solids* **29**, 541 (1968).
- ROTTER C. A. and SMITH C. S., *J. Phys. Chem. Solids* **27**, 267 (1966).
- VORONOV F. F. and VERESCHAGIN I. F., *Physics Metals. Metall.* **11**, 111 (1961).
- HUGHES D. S. and MAURETTE C., *J. appl. Phys.* **27**, 1184 (1956).
- MILLER R. A. and SCHUI E. D. E., *J. Phys. Chem. Solids* **30**, 589 (1969).
- SLATER J. C. *Introduction to Chemical Physics*, p. 450. McGraw Hill, New York (1939).
- GILVARRY J. J., *J. chem. Phys.* **23**, 1925 (1955).

COMMENTS ON THE COMPARISON OF DYNAMIC AND STATIC COMPRESSION DATA*

R. GROVER

Lawrence Radiation Laboratory, University of California, Livermore, Calif. 94550, U.S.A.

(Received 12 January 1970; in revised form 19 February 1970)

Abstract—A detailed discussion is presented of the relationship between dynamic shock wave data at high pressures, acoustic velocity data at low pressures and the static compression data at intermediate pressures reported by Vaidya and Kennedy in the previous paper.

1. INTRODUCTION

IN THE previous paper[1] by Vaidya and Kennedy (VK) it was possible for the first time to make an extensive comparison of the compressions of a number of metals determined by three completely independent experimental methods. The compression data for 16 metals obtained by VK in a static, high-pressure, piston-cylinder apparatus were found to be in agreement with the isothermal compressions calculated from shock wave data up to 45 kbar. Such a comparison is of great importance, for instance, in detecting systematic errors in pressure scales developed in static and dynamic high pressure experiments[2].

The purpose of this note is to identify the shock data used in the comparison by VK and to discuss the validity of extrapolating shock data to low pressures for such a comparison. In connection with this discussion the relationship between measurements of sound velocity at very low pressure and shock velocity data at high pressures is reviewed and a comparison of both kinds of velocity data is made for the metals studied by VK. On the basis of this comparison the consistency between static and dynamic compression data is strengthened.

The reduction of shock compression data on metals to isothermal compression was extensively reviewed in the original survey

article by Rice, McQueen, and Walsh[3]. In this and much of the subsequent work most attention has been given to the reduction of shock data at high pressures and the extrapolation to low pressures was limited to a comparison with the older compressibility data on metals by Bridgman. In a number of these metals low pressure phase transitions are now known and have been detected in shock wave experiments. When no transition is present newer ultrasonic velocity data can now be used in conjunction with high pressure shock data to obtain more accurate compression curves at low pressure. Little thermodynamic equation-of-state information has been extracted directly from shock wave experiments at low pressures in the vicinity of the elastic yield strength because of the more complicated nature of shock wave propagation at low pressures.

2. SHOCK WAVE DATA

Most of the shock compression values quoted by VK are taken from an extensive AIP Handbook tabulation of isothermal compression P - V curves derived from shock data as reported by Keeler[4]. The isotherms were calculated from shock data as fitted in the usual way by a polynomial expansion of the shock velocity U_s in powers of the material or particle velocity U_p ,

$$U_s = C + S U_p + S_2 U_p^2 + \dots$$

The fits used in the handbook tabulation are identified by an asterisk in Table 1 and were

*Work performed under the auspices of the U.S. Atomic Energy Commission.

Table 1. Comparison of shock wave and sonic velocity data

Mat.	ρ_r^* (g/cc)	ρ_0 (g/cc)	Shock				Ref.	Sonic		
			C (cm/ μ sec)	S	S_2 (μ sec/cm)	S_3 (μ sec/cm) ²		C (cm/ μ sec)	S	Ref.
Ag	10.494	10.49	0.322*	1.52			[a]	0.314	1.75	[S1, S2]
Al	2.698	2.78	0.528*	1.50	-0.67	0.41	[b]	0.532	1.48	[S3, S4]
Au	19.302	19.24	0.312*	1.52			[a]	0.300	1.82	[S1, S2]
			0.294	1.87	-1.38		[c]			
Ba	3.65	3.75	0.159	0.88			[d]	0.159		[d]
Ca	1.53	1.56	0.346	0.99			[d]	0.331		[d]
Cd	8.642	8.64	0.238	1.75			[e]	0.237	1.89	[S5, S6]
			0.247*	1.66			[a]			
Cu	8.932	8.90	0.401*	1.47			[a]	0.392	1.62	[S1, S2]
Fe	7.873	7.85	0.460	1.43			[a]	0.460	1.56	[S7, S8]
In	7.286	7.28	0.239*	1.55			[f]	0.239		[S9]
La	6.174	6.135	0.208	1.12			[g]	0.213		[g]
Mo	10.220	10.17	0.514*	1.26			[a]	0.513		[S10, S15]
Ni	8.907	8.86	0.465*	1.45			[h]	0.454		[S11]
Pb	11.341	11.34	0.201*	1.54			[a]	0.199	1.58	[S12, S13]
Sn	7.285	7.29	0.275	1.37			[i]	0.275		[S14]
Ta	16.626	16.67	0.345*	1.20			[a]	0.340		[S15]
Zn	7.134	7.13	0.298*	1.65	-0.26		[a]	0.294		[S16]

[a] VAN THIEL M. and KUSUBOV A. S., *Compendium of Shock Wave Data*, Vol. 1 and 2, UCRL-50108 1966 plus 1967 supplement. Available from Clearinghouse for Federal Scientific and Technical Information, NBS, U.S. Dept. of Commerce, Springfield, Va 22151.

[b] From unpublished fit to LRL shock data on Al2024 and sonic data. The data of G. D. Anderson, D. G. Doran, and A. L. Fahrenbruch on a purer alloy Al 1060 is fit by $0.539 + 1.34 U_p$. Below 50 kbar there is a negligible difference in V/V_0 .

[c] PASTINE D. J. and PIACESI D., *J. Phys. Chem. Solids* **27**, 1783 (1966).

[d] LARSON D. B., *Lawrence Radiation Lab., Livermore*, (private communication). With the use of standard flash gap techniques transition pressures of ~ 180 and 70 kbar were established in Ca and Ba respectively. The reason for the high sample densities relative to X-ray values is not known.

[e] WAISH J. M., RICE M. H., McQUEEN R. G. and YARGER F. L., *Phys. Rev.* **108**, 196 (1957).

[f] McQUEEN R. G. and MARSH S. P., *Los Alamos Scientific Lab. Rep.* No. GMX-6-566 (unpublished)—see also [a].

[g] GUST W. H., *Lawrence Radiation Lab., Livermore*, (private communication), AL'TSCHULER L. V., BAKANOVA A. A. and DUDOI ADOV I. P., *Zh. ETF Pis'ma* **3**, 483 (1966); *Soviet Phys. JETP Lett.* **3**, 315 (1966).

[h] McQUEEN R. G. and MARSH S. P., *J. appl. Phys.* **31**, 1253 (1960).

[i] KARTH J., *Lawrence Radiation Lab., Livermore*, (private communication), a transition was located by a method utilizing an inclined, internally reflecting prism at $U_s = 0.33$, $U_p = 0.038$, or a shock pressure ~ 94 kbars.

[S1] DANIEL S. W. B. and SMITH C. S., *Phys. Rev.* **111**, 713 (1958).

[S2] CHANG Y. A. and HIMMEL L., *J. appl. Phys.* **37**, 3567 (1966).

[S3] SCHMUNK R. E. and SMITH C. S., *J. Phys. Chem. Solids* **9**, 100 (1959).

[S4] VALLIN J., MONGY M., SALAMA K. and BECKMAN O., *J. appl. Phys.* **35**, 1825 (1964).

[S5] CORLI J. A., (unpublished ONR Report #6, June 1962, Case Inst. of Tech.).

[S6] GARLAND C. W. and SILVERMAN J., *Phys. Rev.* **119**, 1218 (1960).

[S7] GUINAN M. W. and BESHER D. N., *J. Phys. Chem. Solids* **29**, 541 (1968).

[S8] LORD A. E. and BESHER D. N., *J. appl. Phys.* **36**, 1620 (1965).

[S9] CHANDRASEKHAR B. S. and RAYNE J. A., *Phys. Rev.* **124**, 1011 (1961).

[S10] BOLEF D. I. and DE KLERK J., *J. appl. Phys.* **33**, 2311 (1962).

[S11] ALERS G. A., NEIGHBOURS J. R. and SATO H., *J. Phys. Chem. Solids* **13**, 40 (1960).

[S12] MILLER R. A. and SCHUELE D. E., *J. Phys. Chem. Solids* **30**, 589 (1969).

[S13] WALDORF D. L., ALERS G. A., *J. appl. Phys.* **33**, 3266 (1962).

[S14] RAYNE J. A. and CHANDRASEKHAR B. S., *Phys. Rev.* **120**, 1658 (1960).

[S15] FEATHERSTONE F. H. and NEIGHBOURS J. R., *Phys. Rev.* **130**, 1324 (1963).

[S16] ALERS G. A. and NEIGHBOURS J. R., *J. Phys. Chem. Solids* **7**, 58 (1958).

summary fits to U_s-U_p data from several laboratories. The data, their source as well as the summary fits are taken from a Compendium of Shock Wave Data (Table 1, Ref. [a]).

A number of the metals investigated by VK have phase transitions with substantial volume changes below 200 kbar. For five of these, Fe, Sn, Ba, Ca and La, some shock data on the low pressure phase are available. The U_s-U_p fits for these metals are also listed in Table 1.

The correction to the shock compression curve for shock heating was calculated in a standard manner by assuming a Mie-Grüneisen γ which depends on the shape of the zero degree isotherm in PV space. The Dugdale-MacDonald relationship for γ was used because of the average agreement with thermodynamic values of γ at low pressure [3]. However, the thermal pressure corrections which depend on gamma are very small at pressures below 45 kbar. For instance, an extreme case is the isotherm of Pb where the thermal offset between the isotherm and Hugoniot should be large because of the low specific heat and high compressibility of this metal. The Dugdale-MacDonald γ in this case is 30 per cent low. Calculations however show that the compression along the 300°K isotherm is increased by only 2 per cent if gamma is increased by 40 per cent.

Another source of differences between static and shock compression data arises from the different reference density used in each method. The compression calculated from a shock velocity measurement in a sample by the usual conservation relation is strictly speaking relative to the initial bulk density of the sample. In the static compression method the reference density is that of the sample after several preliminary compression cycles which is presumed to be the

X-ray density of the material. Table 1 lists typical initial densities ρ_0 for samples used in shock wave experiments which were used to calculate pressures and compressions. It can be seen that many are several tenths of a per cent lower than the X-ray densities listed in the table. Because the Hugoniot pressure is proportional to ρ_0 , the resulting error in the calculated shock pressure is negligible. The error in compression due to ρ_0 is larger and more difficult to estimate. It is of the order of the deviation from X-ray density divided by the mean density change over the range of shock measurements and is proportional to the Grüneisen γ in the same compression range. Since shock wave data is taken in a range of compressions typically from 15 to 35 per cent, the calculated compression is larger than that of a dense solid by a small amount of the order of 1-2 per cent. Note that this error is similar in magnitude to the random errors in the measurement of shock velocities and is usually ignored.

3. COMPARISON OF SONIC AND SHOCK DATA

The extrapolation of Hugoniot data to low pressures is best evaluated by comparing with ultrasonic data. The ideal $P-V$ Hugoniot for a material of zero strength coincides in slope and curvature with the isentrope (locus of constant entropy) through the initial state. Therefore if material strength effects are very small, the 'bulk' sound speed calculated from the isentropic bulk modulus, B_s , should be equal to C and the linear shock velocity coefficient, S , should be determined by the pressure derivative of B_s along an isentrope.

$$S = \frac{1}{4} \left[\left(\frac{\partial B_s}{\partial P} \right)_s + 1 \right].$$

A large amount of more accurate ultrasonic

* Fits used in Ref. [4].

† TAYLOR A. and KAGLE G. J., X-ray densities taken from *Crystallography Data on Metal and Alloy Structures*, Dover, New York (1963); with the exception of Mo which was calculated from crystal constants in WYKOFF R. W. G., *Crystal Structures*, 2nd Edn. Interscience, New York (1963).

data has become available in recent years and a tabulation of the ultrasonically derived coefficients C and S for metals is also listed in Table 1. $(\partial B_s/\partial P)_s$ is evaluated by means of the thermodynamic relation

$$\left. \frac{\partial B_s}{\partial P} \right|_s = \left. \frac{\partial B_s}{\partial P} \right|_T + \gamma \alpha T \left. \frac{\partial \ln B_s}{\partial \ln V} \right|_P$$

from the measurements of sound velocity changes with both changes in pressure and temperature. An experimental uncertainty of ≤ 1 per cent can be assigned to C judging by agreement between different experimentalists. On the same basis, however, the experimental uncertainty in S is ~ 10 – 20 per cent. The tabulated sonic data on S are from sonic velocity measurements over a pressure range of several kilobars or more.

Among the metals without low pressure phase transitions there is generally a satisfactory agreement between the two dynamic determinations of C , to ≤ 2 per cent. The value determined from shock data on Ag, Au, Cu, and from the summary data fit for Cd exceed the ultrasonic values of C by a somewhat larger amount. In these cases the shock values of S are also lower than usual. Pastine and Piacesi[5] have suggested that this is due to curvature in the Hugoniot at low pressures. They fit shock data on the noble metals to a quadratic U_s-U_p relation holding C fixed at an earlier ultrasonic value. Considerably closer agreement with sonic values of S was found as shown for example in the table for Au. In the case of Cd the shock wave data itself gives evidence of a similar curvature at low pressures. Table 1 contains a fit to lower pressure shock data on Cd which is in good agreement with sonic data. This fit was used for the comparison with static data in the previous paper.

The dynamic compression data on low pressure phases of Ba, Ca and La consists of a small number of Hugoniot points and sound velocity measurements on a polycrystalline sample. The disagreement between the fits

to the shock data and the bulk sound speed in Ca and La are not inconsistent in view of the sparsity of the Hugoniot data. VK find that for Ca the agreement between the shock-derived isothermal compression and static measurements is excellent while in the case of La the disagreement (~ 5 per cent) is the largest of all the metals.

It should be noted here that the shock velocity 'fits' listed in Table 1 for the low pressure phases of Fe and Sn were obtained from measured ultrasonic velocities and shock data at the transition pressure. In the case of Fe, there is extensive but anomalous shock data below 100 kbar on the low pressure phase, which is not adequately understood[6].

Although there is good overall agreement between sonic and extrapolated shock wave velocities at low pressure there is still room for improvement in the agreement by means of material strength corrections. For instance, the above indications of a non-linear U_s-U_p relation in a few metals can also be explained as a strength effect. In addition, although the ultrasonic value of S is not very reliable for some metals, Table 1 indicates that there may be a more widespread difference between sonic and shock wave values of S among the metals. At high pressures ($\geq \frac{1}{2}$ bulk modulus) one may be sure that the strength correction becomes negligible for two reasons. Judging by data on a wide variety of solids at normal densities yield strength should be a fraction of 1 per cent of the bulk modulus. Secondly the yield strength must drop quickly as shock heating brings the metal near the melting temperature. The above agreement between sonic and shock velocities at low pressures suggests that in metals the correction for material strength is small down to much lower pressures. For other types of solids (i.e. ceramics, rocks, etc.) of high yield strength there are discrepancies between sonic and shock data indicating that significant corrections are needed[7]. It is to be hoped that the extensive experimental work being done presently on shock propagation at very low pressures[8]

will clarify the questions about the importance of the strength correction in metals at lower pressures.

4. DISCUSSION AND CONCLUSION

Within the qualifications discussed above it has been shown that the extrapolation shock velocity data for most metals to zero pressure is consistent with sound velocity data to within ~ 2 per cent, comparable with the accuracy of the shock velocity data itself. Therefore the shock compression data is suitable for comparison with the static data of VK in the intermediate pressure range. Except for La the agreement found by VK between the two sets of compression data is everywhere consistent within an experimental error of several tenths of a percent in the static volume measurements and of 2 per cent in the shock compression measurements. It may thus be concluded that all three types of compression data are consistent up to 45 kbar.

Discrepancies between the isothermal compressibility calculated from fits to the static data of VK and from sound velocity data in some metals are apparently not real. In the case of Fe, Rotter and Smith[2] have also noted the differences between the compressibility obtained from sonic velocity data and fits to Bridgman's data. Such differences have usually been attributed to a loss of accuracy in taking differences between volume measurements in the static compression method. These discrepancies may also in part be due to inappropriate methods of fitting or representing static data. In this connection it

should be noted that the simple U_s-U_p expansion used to fit shock wave data over a much larger range of pressures implies a volume dependence of the pressure along the isotherm which is different from either the Bridgman or Murnaghan form used by VK.

Acknowledgements—Appreciation is due Professor Kennedy for the opportunity to participate in this review of compression data. I would also like to thank R. N. Keeler and E. B. Royce for advice and comments, and D. B. Larson, W. H. Gust, and J. Karth for the use of their unpublished data.

REFERENCES

1. VAIDYA S. N. and KENNEDY G. C., *J. Phys. Chem. Solids* **31**, 3255 (1970).
2. DRICKAMER H. G., LYNCH R. W., CLENDENEN R. L. and PEREZ-ALBUERNE E. A., *Solid St. Phys.* **19**, 135 (1966). ROTTER C. A. and SMITH C. S., *J. Phys. Chem. Solids* **27**, 267 (1966). ANDERSON O. L., *J. Phys. Chem. Solids* **27**, 547 (1966). GROVER R., KEELER R. N., ROGERS F. J. and KENNEDY G. C., *J. Phys. Chem. Solids* **30**, 2091 (1969).
3. RICE M. H., McQUEEN R. G. and WALSH J. M., *Solid St. Phys.* **6**, 1 (1958).
4. KEELER R. N., *American Institute of Physics Handbook*, (Edited by M. Zemansky) in Section on Compressibilities (1970) in press.
5. PASTINE D. J. and PIACESI D., *J. Phys. Chem. Solids* **27**, 1783 (1966).
6. KEELER R. N. and MITCHELL A. C., *Solid State Commun.* **7**, 271 (1969).
7. AHRENS T. J., GUST W. H. and ROYCE E. B., *J. appl. Phys.* **39**, 4610 (1968).
8. See for example: MUNSON D. E. and BARKER L. M., *J. appl. Phys.* **37**, 1652 (1966). TAYLOR J., *Dislocation Dynamics* (Edited by Alan R. Rosenfeld, G. T. Hahn, A. L. Bement and R. I. Jaffee), McGraw-Hill, New York (1968). See also reports by GRAHAM R. A. and VAN THIEL M., *Proc. Symp. Accurate Characterization of High Pressure Environment, Gaithersburg, Maryland*, October 14–18 (1968).

PROPERTIES OF THIN FILMS OF ZINC OXIDE PREPARED BY A CHEMICAL SPRAY METHOD

J. McK. NOBBS and F. C. GILLESPIE

Australian Defence Scientific Service, Defence Standards Laboratories, Department of Supply,
Adelaide, Australia

(Received 18 February 1969; in revised form 1 December 1969)

Abstract—The electrical, optical and structural properties of thin films of zinc oxide in the thickness range 10–400 nm on glass and fused quartz substrates have been investigated. The films were prepared using a new chemical spray technique which permitted deposition on either insulating or conducting substrates with a high degree of control over both the dimensions of the coatings and their electrical properties. The effects of variations in film thickness and heat treatment in oxygen have been examined and an assessment has been made of the dimensions of the depletion layer and of the diffusion coefficient of interstitial zinc in zinc oxide. Films with thicknesses greater than 40 nm are stable for long periods and show a crystalline structure with a preferred orientation of the *c*-axis normal to the substrate. An amorphous phase together with crystallites is apparent in films less than 40 nm thick. However, these films are unstable and show crystallite growth after storage at room temperature. In general, the optical properties of the films correspond with those of films prepared by other methods.

1. INTRODUCTION

Thin films of zinc oxide can be prepared by vacuum evaporation of the metal followed by oxidation[1]. However, difficulty is usually experienced in obtaining good adhesion of the films to the substrate. High quality thin films are more readily obtained by sputtering zinc in oxygen at low pressures[2]. However, the process is slow and several hours are required for a film thickness of 500 nm.

Thin films of zinc oxide with a large surface area (20 cm²) with controlled thickness and conductivity were required for the study of surface reactions between zinc oxide and ambient gases. Considerable difficulty was experienced in preparing such films by vacuum evaporation or sputtering; in the latter case residual gases in the vacuum system, particularly hydrocarbons, had a deleterious effect on their surface properties.

Chemical spray techniques have been used successfully for preparing conductive layers of tin oxide[3] and thin films of II–VI compounds[4], particularly cadmium sulphide [5].

This paper describes the properties of thin

films of zinc oxide prepared by use of a chemical spray technique. In principle the preparation method required a soluble zinc compound which would decompose into zinc oxide at substrate temperatures of less than 500°C. This temperature was set by the fact that glass substrates were preferred for the study of surface reactions. A number of zinc compounds in various solvents were investigated, the best results being obtained with an aqueous solution of zinc acetate.

The chemical spray method permitted a high degree of control to be exercised over the properties of the coatings and produced films which were satisfactory both for the investigation of surface reactions and for the study of the various properties of polycrystalline zinc oxide including the dimensions of the depletion layer and the diffusion of interstitial zinc.

2. PREPARATION OF FILMS

The films were prepared on glass, fused quartz and aluminium substrates (25 × 75 × 1 mm) which were placed on a metal block and heated to 500 ± 20°C. A saturated aqueous

solution of zinc acetate was sprayed on to the substrates using a conventional spray gun with a high air to solution ratio. The spray was applied in 1 sec bursts allowing time for the substrate temperature to recover after each application. Film thicknesses were determined by weighing and ranged between 10–500 nm. Variation of thickness over the surface amounted to less than 10 per cent. Analysis of the coatings showed that their residual zinc acetate content was less than 0.01 per cent which could be further reduced by baking in oxygen at 350°C at atmospheric pressure.

3. FILM STRUCTURE AND ORIENTATION

The structures and orientations of films ranging in thickness between 20–300 nm were examined by optical and electron microscopy and by X-ray diffraction.

The films, when first produced, were generally glass clear and free from macroscopic defects. However, on standing for periods of more than a week, films with thicknesses of less than 40 nm tended to develop translucent areas which in some cases covered up to 25 per cent of the total film area. Microscopic examination showed that the translucent areas resulted from the formation of crystallite needles, averaging $2\mu\text{m} \times 40\mu\text{m}$, which had grown on the film without separating from the substrate. An example of such a structure is shown in Fig. 1. Electron microscopic examination of the darker areas surrounding the crystallites, as shown in Fig. 1, revealed the presence of a thinner secondary film with possibly an amorphous structure. Films with thicknesses greater than 40 nm were stable and have been stored for long periods without deterioration.

The results of X-ray diffraction analysis showed that films thicker than 60 nm possessed a crystalline structure with a preferred orientation of the *c*-axis normal to the substrate. Below 60 nm no evidence of structure was recorded. The results of electron microscopy

supported those from X-ray diffraction and showed crystalline structure in films with thicknesses down to 40 nm. However, the results on films below this thickness were inconclusive with evidence of both amorphous and crystalline phases in their structure; an electron micrograph of such a film is shown in Fig. 2.

The dimensions of the crystallites in the films varied between 5–30 nm with the size increasing approximately linearly with film thickness. The degree of orientation of the *c*-axis varied between films and also between different areas on the same film. The cause of this variation has not been fully determined but appears to arise from thermal gradients within the substrate caused by the spraying technique.

Electron micrographs of films of two thicknesses showing typical crystallite structure and orientation are reproduced in Figs. 3 and 4.

4. ELECTRICAL AND OPTICAL MEASUREMENT

Ohmic gold electrodes were applied to the films by vacuum evaporation. The electrodes were in the form of an interlocking comb pattern giving an effective electrode length of 45 cm and a separation of 500 μm . With 1.5 V d.c. potential applied to the electrodes cell currents ranged between 10^{-11} and 10^{-2} A. The currents were measured with an electrometer amplifier.

The slides were mounted in a shielded container, with a window for illumination of the films, and provision was made for the admission of various gases. Cell currents were measured at equilibrium after each change in conditions. In dry air and in dry oxygen, equilibrium values for both dark conductivities and photoconductivities were not reached even after several days of either dark resting or illumination. However, as outlined in a previous paper[6], water vapour has the effect of accelerating photoconductivity rise and decay kinetics and by using air at 50 per cent relative humidity,



Fig. 1. Micrograph of 20 nm film ($\times 30$) Showing crystallite growth pattern in translucent areas of film

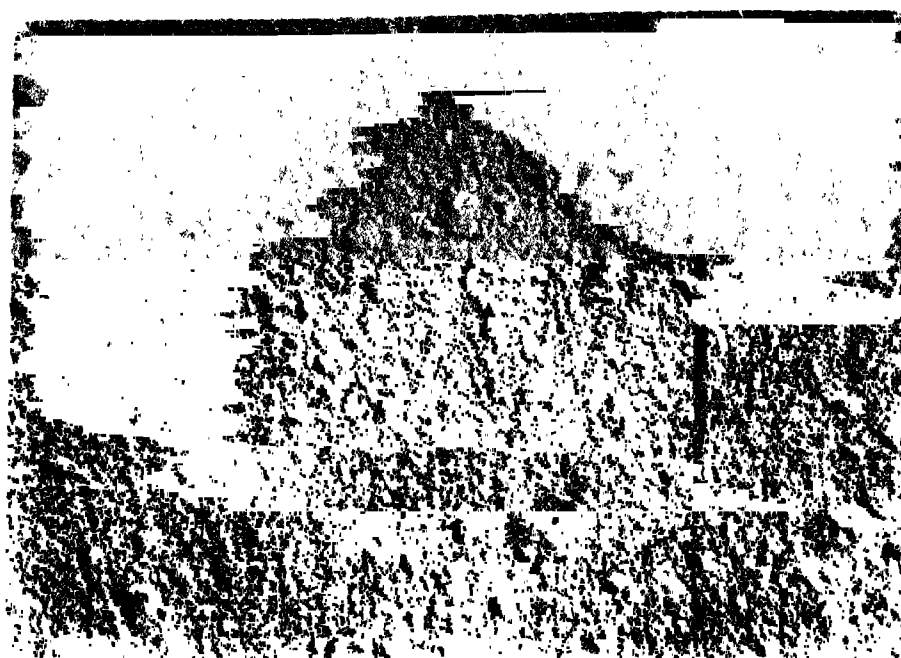


Fig. 2. Electron micrograph of 20 nm film ($\times 40,000$) showing structure of "Clear" areas of film. Particle size in basic structure is less than 5 nm, with crystallites on surface.

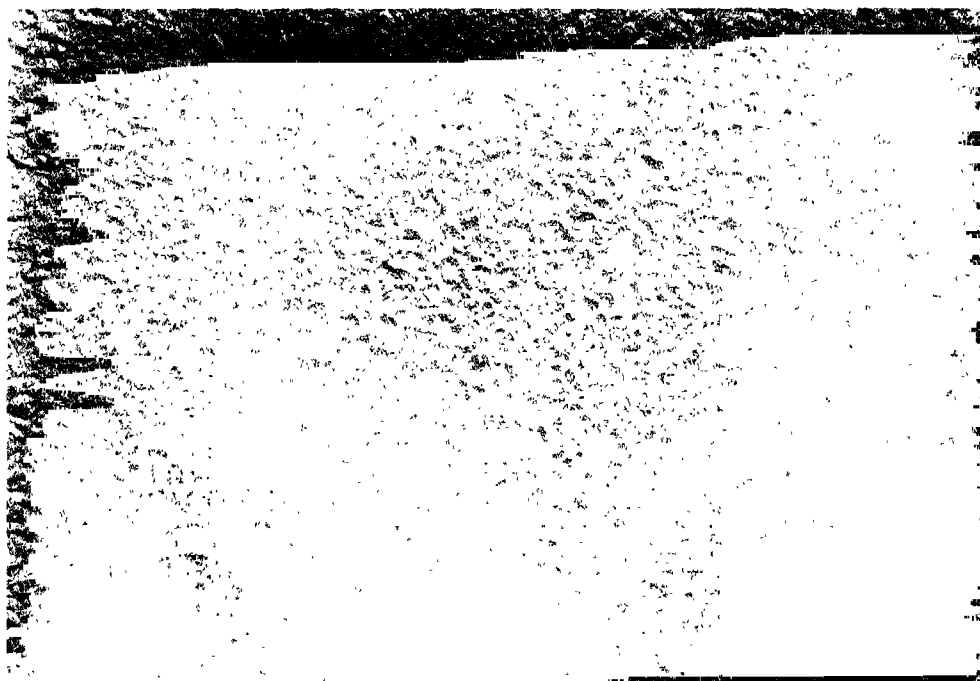


Fig. 3. Electron micrograph of 60 nm film ($\times 40,000$). Showing typical structure of films. Crystallite size approx. 5 nm

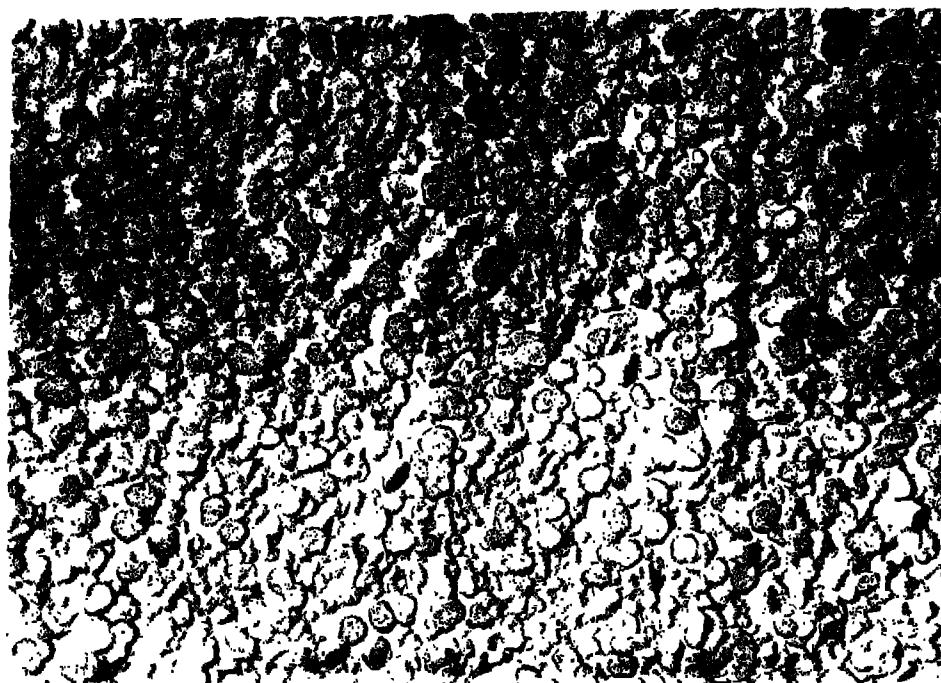


Fig. 4 Electron Micrograph of 130 nm film ($\times 40,000$) Showing preferred c -axis orientation in thicker films. Crystallite size approx. 10 nm

equilibrium values could be obtained in less than one hour.

For measurement of photoconductivity the cells were illuminated with unfiltered light from a 150 W quartz-iodine lamp, the active areas of the cells receiving 100 mW of radiation. For the measurement of spectral response, light from a 150 W xenon arc lamp was dispersed in a high aperture prism monochromator with glass optics. No correction was made for the spectral output of the lamp or for the dispersion characteristics of the monochromator. A spectrophotometer covering the wavelength range 200–1200 nm was used for the optical transmission measurements.

For films less than 40 nm thick, which tended to show crystallite growth after storage, both the electrical and optical measurements were made before the onset of crystallization.

5. RESULTS AND DISCUSSION

(a) *Spectral transmission*

Figure 5 shows the spectral transmission curves of films of zinc oxide on fused quartz; the transmission measurements being made relative to the substrate. The prominent features of the curve are the absorption edge at 380 nm and the narrow absorption maximum at 365 nm. These correspond to photon energies of 3.28 and 3.42 eV respectively.

The flattening of the curves below 365 nm and the shallow absorption peak at 210 nm correspond with the results obtained by Mickelson and Kingery[2] on amorphous zinc oxide films. The results in Fig. 5 therefore suggest the presence of both amorphous and crystalline phases in films less than 40 nm thick. Some evidence relative to this type of structure is shown in Fig. 2.

Figure 6 shows the variation in transmission with thickness of the films at the wavelengths specified. Analysis of the results gave values for absorption coefficients of 6×10^5 at 365 nm and 2×10^4 at 380 nm. Those results agree closely with those previously reported[1].

(b) *Conductivity*

Figure 7 shows the variation in dark conductivities and photoconductivity with thickness of films in both the baked and unbaked conditions. The conductivities were calculated using the spacing between the electrodes on the surface, together with the thicknesses of the films, as the conduction path. It is well known[7] that chemisorption of oxygen on zinc oxide forms a depletion layer at the surface with a conductivity many times lower than that of the bulk. Accordingly, where the depth of this layer has the same dimensions as the thickness of the films, the conductivity will be determined by the surface properties and it can be seen that the depth of the depletion layer apparently extends to about 100 nm. As the thickness increases the bulk conductivity becomes the controlling factor. Figure 7 shows that the dark conductivities of the films increase rapidly with thickness up to a particular value and then decrease. This suggests that a limiting value is reached equivalent to that of the bulk conductivity. The apparent decrease in dark conductivity with increasing film thickness is due to the surface electrode geometry used, as the carrier flow paths are concentrated near the surface and consequently the conduction path is not proportional to film thickness above a particular value.

With unbaked films the conductivity rises rapidly with film thickness which follows from the existence of both a depletion layer at the surface and, below this layer, a region of high conductivity which approaches the bulk value. The photoconductivity, on the other hand, is not so dependent on thickness which results from the fact that 90 per cent of the incident photons are absorbed in the depletion layer.

The results obtained on baked films show a 4 order decrease in dark conductivity compared with unbaked films; this is due to the fact that a high proportion of the interstitial zinc donors is removed during the baking process through diffusion to the

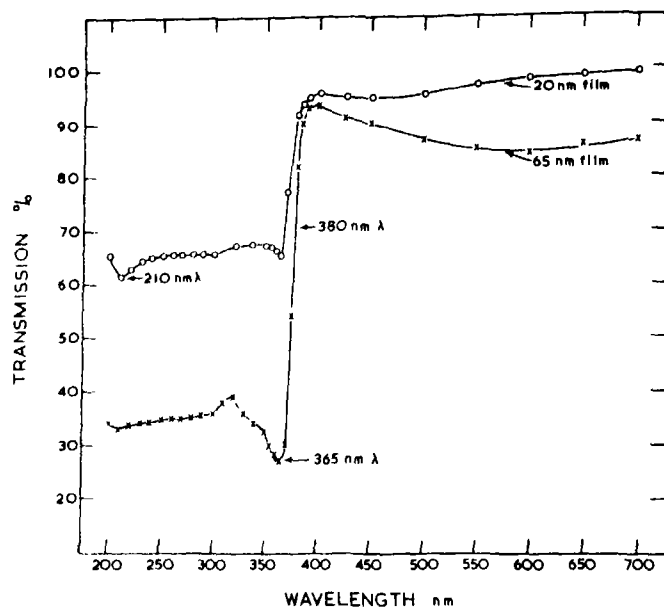


Fig. 5. Transmission against wavelength of thin films of zinc oxide. Film thicknesses 20 and 65 nm.

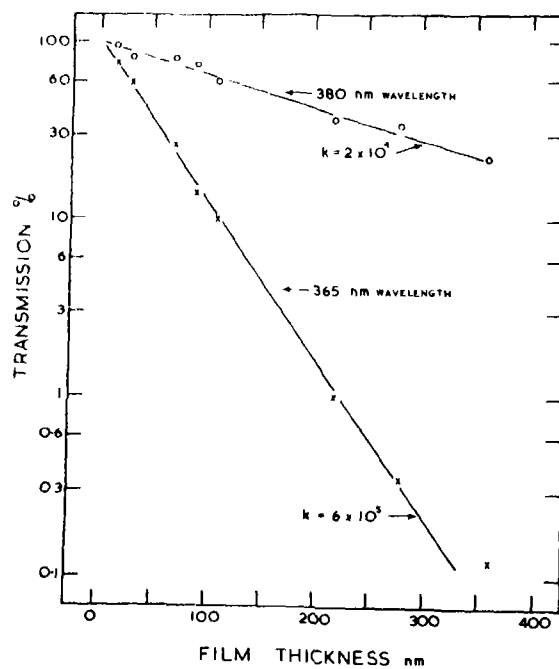


Fig. 6. Transmission against thickness of ZnO films at 365 and 380 nm wavelengths.

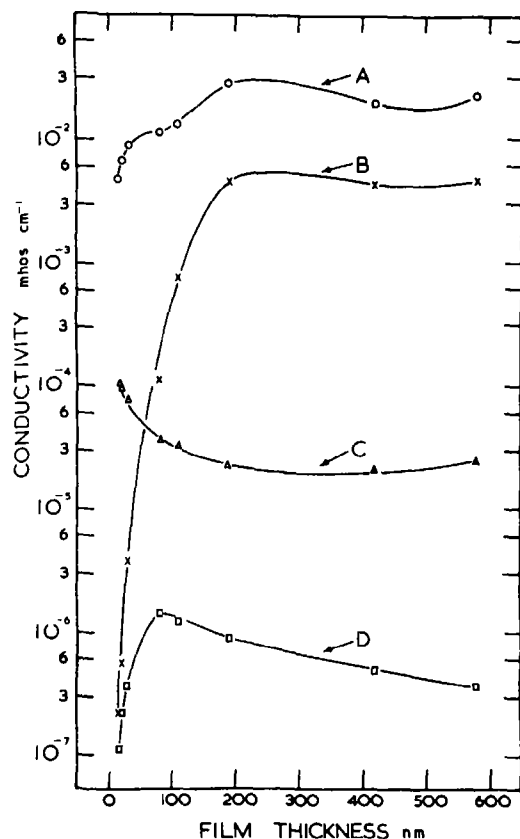


Fig. 7. Conductivity against thickness of ZnO films. A. Photoconductivity of unbaked films. B. Dark conductivity of unbaked films. C. Photoconductivity of films baked for 30 min in oxygen at 350°C. D. Dark conductivity of films baked for 30 min in oxygen at 350°C.

surface and subsequent oxidation[8,9]. Baked films also show a depletion layer although its effect is not so pronounced since the bulk conductivity is significantly lower relative to the unbaked films and approaches that of the depletion layer. Photoconductivity in the baked films shows a decrease with film thickness indicating again that photons of band gap energy are largely absorbed in the 100 nm distance below the surface.

Another possible explanation for the rapid increase in dark conductivity with film thickness is the effect described by Mickelsen

and Kingery[2] in which films showing an amorphous structure have conductivities 4 to 5 orders lower than similar films with a crystalline structure. The increase in conductivity of the sprayed films could therefore be ascribed to an increase in the ratio of crystalline to amorphous phases which was in evidence in Figs. 2 and 5.

The results in Fig. 7 also show that the maximum photoconductivity to dark conduc-

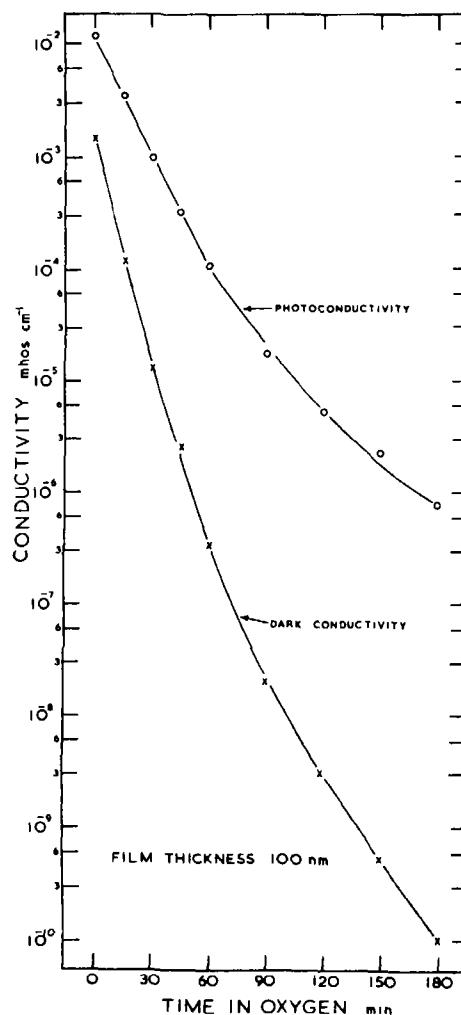


Fig. 8. Variations in dark and photoconductivity of 100 nm film with time of baking in oxygen at 350°C.

tivity ratio is obtained in films with high donor concentrations, but which are thinner than the depletion layer formed by chemisorption of oxygen. Baking in oxygen decreases the p.c./d.c. ratios for thin films but increases it for thicknesses above 150 nm, this variation arises from the four order decrease in bulk conductivity caused by baking.

Figure 8 shows the effect of baking in oxygen on both the dark and photoconductivity of a film 100 nm thick. As shown,

the dark conductivity can be decreased by over 7 orders of magnitude while the decrease in photoconductivity is only 4 orders. Therefore, there is an apparent gain of 10^3 in p.c./d.c. ratio.

However, this gain may not be significant since it has been found that, in addition to the photodesorption reaction which is basically responsible for photoconductivity, photolysis of zinc oxide to zinc and oxygen proceeds during irradiation particularly in the absence of water vapour[6]. While the photolysis

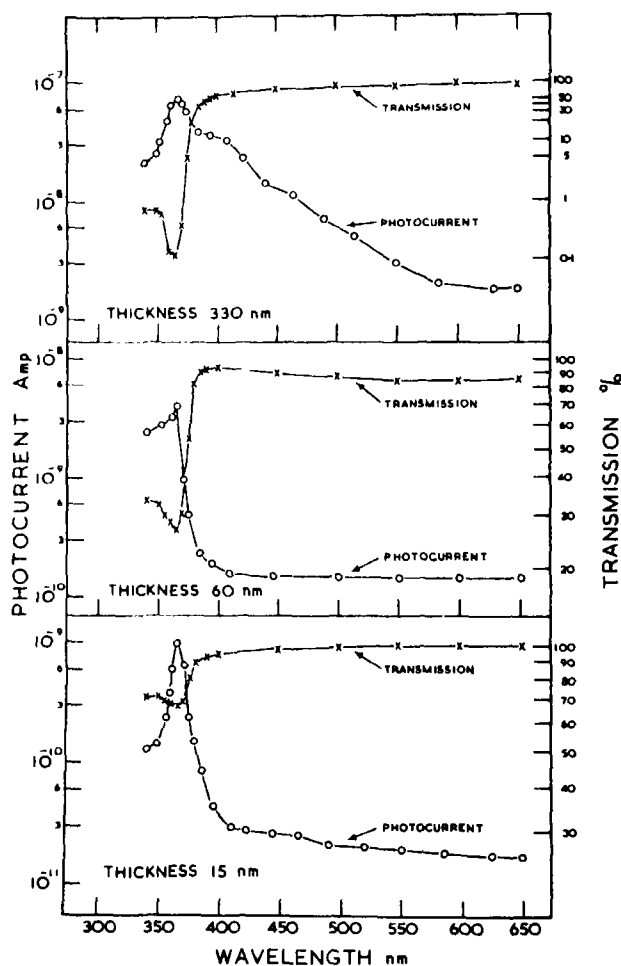


Fig. 9. Spectral photo-response and transmission of unbaked films.

effect has been largely inhibited by the addition of water vapour to the atmosphere it probably remains significant at values of photoconductivity of less than 10^{-5} mhos cm^{-1} .

Assuming that the donors in zinc oxide are interstitial zinc atoms and that their concentration is reduced by oxidation at the surface during the baking procedure[8,9], then the results in Fig. 8 can be used to give an estimate of the diffusion coefficient of zinc in zinc oxide at the temperature of baking, 350°C . Calculations from these results give a value of $D = 2.4 \times 10^{-14} \text{ m}^2 \text{ sec}^{-1}$. This compares with the results published by Thomas[10] viz. $D = 4.2 \times 10^{-13} \text{ m}^2 \text{ sec}^{-1}$ at 300°C , and by Moore and Secco[11] viz. $D = 1.58 \times 10^{-16} \text{ m}^2 \text{ sec}^{-1}$ at 1000°C . Further experimental work is being carried out to determine the feasibility of using this method to investigate diffusion characteristics in thin films of zinc oxide.

Figure 9 shows the spectral response curves of three films with thicknesses 15, 60 and 330 nm respectively and, for comparison, their spectral transmissions. It is seen that for the two thinner films the spectral response follows closely the photon absorption with very little response above 390 nm,

while the peak occurs at 365 nm. The photo-response is appreciably higher at longer wavelengths in the thickest film and this is accompanied by a higher photon absorption at these wavelengths. However, the photo-response is not proportional to thickness at wavelengths greater than 400 nm and it is apparent that some other factor is involved. It is possible that carriers generated within the bulk have longer lifetimes than those generated near the surface.

Acknowledgements—The authors are indebted to Mr. H. R. Limb for the optical and electron micrographs of the thin films.

REFERENCES

1. HEILAND G., MOLLWO E. and STOCKMAN F., *Solid St. Phys.* **8**, 191 (1959).
2. MICKELSON R. A. and KINGERY W. D., *J. appl. Phys.* **37**, 3541 (1966).
3. LIBBEY-OWENS-FORD GLASS Co., *Brit. Pat.* **682**, 342 (1949).
4. SHALLCROSS F. V., *RCA Rev.* **28**, 569 (1967).
5. CHAMBERLIN R. R. and SKARMAN J. S., *J. electrochem. Soc.* **113**, 86 (1966).
6. NOBBS J. McK., *J. Phys. Chem. Solids* **28**, 205 (1968).
7. MELNICK D. A., *J. chem. Phys.* **26**, 1136 (1957).
8. THOMAS D. G., *J. Phys. Chem. Solids* **9**, 31 (1959).
9. NORMAN V. J., *Aust. J. Chem.*, **19**, 1133 (1966).
10. THOMAS D. G., *J. Phys. Chem. Solids* **3**, 229 (1957).
11. SECCO E. A. and MOORE W. J., *J. chem. Phys.* **26**, 942 (1957).

QUASIELASTIC NEUTRON SCATTERING BY HYDROGEN IN NIOBIUM

W. GISSLER*, G. ALEFOLD and T. SPRINGER

Institut für Festkörper- und Neutronenphysik der Kernforschungsanlage Jülich GmbH, Jülich, Germany

(Received 2 September 1969; in revised form 13 October 1969)

Abstract—The diffusion of hydrogen in niobium has been studied by quasielastic neutron scattering measuring the width of the quasi-elastic line as a function of the scattering vector. The measurements have been performed at concentrations of 3.2 at.% at 200° and 300°C, and at 33 at.% hydrogen between 100° to 300°C for many temperatures, especially close to the critical point at about 150°C. The diffusion constant at 33 per cent changes between $D = 2.7 \cdot 10^{-5} \text{ cm}^2/\text{sec}$ at 310°C and $0.8 \cdot 10^{-5} \text{ cm}^2/\text{sec}$ at 120°C. Experiments at small and large scattering vectors are indicative for a octahedral jump model in the temperature region above T_c . An anomaly has been observed in the line width for large scattering vectors as well as in the Debye-Waller factor at temperatures close to the critical temperature.

1. INTRODUCTION

IN NIOBIUM, as in various other metals, hydrogen has a very high solubility. The protons occupy interstitial sites and interchange their positions at a rate which for niobium is comparable with or even higher than that of atoms in ordinary liquids. For the b.c.c. lattice of niobium two possible interstitial positions have been suggested: octahedral or tetrahedral sites (Fig. 1).

The similarity of the phase diagram of this system [1] (Fig. 2) with that of a real gas suggests the existence of a protonic 'lattice gas' (α -phase) and a 'lattice liquid' (α' -phase) [2]. The boundary of the miscibility gap in Fig. 2 thus can be considered as the coexistence curve between the lattice gas and the lattice liquid. Hydrogen in niobium therefore can, to a first approximation, be considered as an example of a lattice gas which in itself and by virtue of its analogies to other continuous phase-transitions like ferromagnetism is of great theoretical interest. The aim of this paper is the investigation of those dynamical

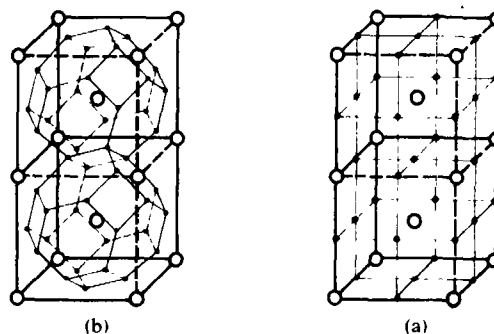


Fig. 1. Octahedral (a) and tetrahedral (b) positions in a b.c.c. lattice. The jump distance is $s = a/2$ for (o-o) jumps, and $s = a\sqrt{2}/4$ for (t-t) jumps (a = edge length of the cubic cell).

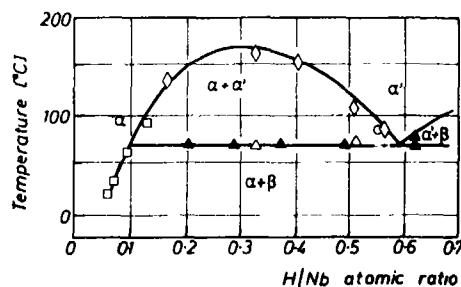


Fig. 2. Phase diagram of hydrogen in niobium (from [1]).

*Present address: Euratom, Forschungsanstalt, Petten, the Netherlands.

properties of the lattice gas which can be studied by incoherent neutron scattering.

Neutron scattering as a tool to investigate the diffusion of protons in solids has been applied for the first time to solids by Sköld and Nelin[3] and Verdan *et al.*[4] (translational diffusion) and by Stockmeyer and Stiller[5] (rotational diffusion). For protons which are harmonically bound in a solid the energy spectrum of incoherently scattered neutrons shows a sharp line at energy transfer $\hbar\omega = 0$ (similar to the Mössbauer line) in addition to the spectrum caused by inelastic processes. For diffusing protons, however, the line at $\hbar\omega = 0$ has a finite width ('quasi-elastic line'). By analyzing this width as a function of momentum transfer the diffusion constant D , the mean time between jumps τ , and therefore, the jump distance can be extracted. Neutron scattering based on a jump diffusion model has been treated theoretically for the case of a periodic lattice by Chudley and Elliott[6] and by Blaesser and Peretti[7].

Experimental investigations to study jump times of protons in Nb have been performed by Zamir and Cotts[8] by means of nuclear magnetic resonance. Since in the α and α' phase (Fig. 2) which we are interested in, the jump frequencies are about 10^{12} per second compared to 10^7 of the NMR Larmor frequency, this technique loses its reliability. Furthermore, several attempts have been published to determine the jump frequency by internal friction based on the Snoek-effect[9, 10]. However, it has not been established conclusively that the observed internal friction peaks can be attributed to jumps of free protons. The diffusion constant of protons and deuterons in niobium has been studied recently by means of a new elastic relaxation process caused by long range proton diffusion[11]. It will be shown that these measurements are consistent with the neutron scattering results of this work. Quasielastic scattering experiments by Verdan *et al.*[4] have been performed on niobium with 9 per cent hydrogen at 200°C.

In this paper measurements at low concentration (3.2 per cent) where the interaction between the protons is small, and at the critical concentration (33 per cent) for many temperatures between 100° and 300°C will be presented. Most of the data were taken at 33 per cent. To eliminate the influence of impurities and crystal imperfections on the proton diffusion, special attention was paid to careful sample preparation. The main objectives of this work were the investigation of the diffusion constant and the mean jump frequency as a function of temperature and especially close to the critical point, and furthermore information can be obtained concerning the type of interstitial positions.

2. THEORY

Neutron scattering by protons is predominantly incoherent (the bound cross section for incoherent scattering is $\sigma_{inc} = 79.6$ barn, compared to $\sigma_{coh} = 1.78$ barn). Under these circumstances the scattering cross section per solid angle element $d\Omega$ and per energy interval dE , can be written as [12]:

$$\frac{d^2\sigma}{d\Omega dE} = \frac{1}{\hbar} \left(\frac{k}{k_0} \right) \left(\frac{\sigma_{inc}}{4\pi} \right) S_{inc}(\kappa, \omega) \quad (1)$$

$\hbar\omega = E_0 - E = (\hbar^2/2m)(k_0^2 - k^2)$, and $\hbar\kappa = \hbar(\mathbf{k}_0 - \mathbf{k})$ are the energy and momentum transfer during the scattering process. The scattering law, $S_{inc}(\kappa, \omega)$ can be calculated by a Fourier transform of the self correlation function $G_s(\mathbf{r}, t)$ of the scattering proton. This function measures the probability that a proton, being at the time $t = 0$ at the position $\mathbf{r} = 0$ will be at a later time t at a point $\mathbf{r}$. Thus

$$S_{inc} = \frac{1}{2\pi} \iint e^{i(\kappa\mathbf{r} - \omega t)} G_s(\mathbf{r}, t) d\mathbf{r} dt \quad (2)$$

For a qualitative discussion of the scattering law for H in Nb we first make use of the theory of Chudley and Elliott[6]. In this diffusion

theory it is assumed that protons perform jumps of a given length, that successive jumps are independent of each other, that the jumping probability is not influenced by the presence of the other protons, and that the mean time of flight can be neglected compared to the mean time of stay. Therefore, the following rate equation holds

$$\frac{\partial P(\mathbf{r}, t)}{\partial t} = \frac{1}{n\tau} \sum_{\mathbf{s}_j} [P(\mathbf{r} + \mathbf{s}_j, t) - P(\mathbf{r}, t)] \quad (3)$$

P is the probability of finding a particle at $\mathbf{r}$, the vectors $\mathbf{s}_j$ are describing the direction and distance of the possible jumps, n is the number of such vectors, and τ is the mean time of stay. In this equation it is assumed that each site has the same set of jump-vectors $\mathbf{s}_j$. $G_s(\mathbf{r}, t)$ is a solution of (3) with the boundary condition $G(\mathbf{r}, 0) = \delta(\mathbf{r})$.

From this rate equation a Lorentzian scattering law is obtained

$$S_{\text{nc}}(\kappa, \omega) = \frac{f(\kappa)/\pi}{\omega^2 + f^2(\kappa)} \quad (4)$$

$$f(\kappa) = \frac{1}{n\tau} \sum_{\mathbf{s}_j} (1 - e^{i\kappa \cdot \mathbf{s}_j}) \quad (5)$$

The halfwidth therefore is $\Delta E = 2\hbar f(\kappa)$.

In contrast to the assumptions of equation (3), in a b.c.c. lattice all interstitial sites are not equivalent with regard to their jump vectors $\mathbf{s}_j$. For the case of jumps between octahedral positions (*o-o model*) there are three types of position and therefore one obtains three coupled rate equations instead of equation (3). For jumps between tetrahedral sites (*t-t model*) six rate equations are necessary [7]. It has been shown that as a consequence the scattering law consists of a sum of six Lorentzians like equation (4) with, in general, six different halfwidths [7]. All these are periodic functions of $\kappa \mathbf{s}_j$ like equation (5), the periodicity being the same for a given orientation of κ . For a polycrystalline sample, the scattering law has to be averaged over

space. Gissler and Rother [13] recently have determined the self-correlation function for proton diffusion in niobium, solving the rate equation by a random walk technique. Figure 3 shows the results for the halfwidth of the quasielastic line for a polycrystal as a function of κ for both jump models. The oscillatory behaviour of the halfwidth for large κ still exists after the directional averaging. In the case of the octahedral model the asymptotic

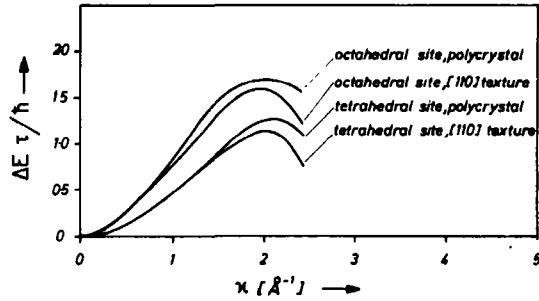


Fig. 3. Halfwidth ΔE of quasielastic line times mean time of stay τ vs. the absolute value of the scattering vector κ for the (*t-t*) and (*o-o*) jump model (from [13]).

value of $\Delta E\tau/\hbar$ for very large κ appears to become smaller than 2 which is the asymptotic value in an isotropic jump model [6]. Gissler and Rother [13] show, that for $\kappa a \ll 1$ the following expressions hold:

$$\Delta E = \frac{2\hbar\kappa^2 a^2}{48\tau} \quad (6a) \quad (t-t \text{ model})$$

$$\Delta E = \frac{2\hbar\kappa^2 a^2}{24\tau} \quad (6b) \quad (o-o \text{ model})$$

Equations (6a) and (6b) agree with Vineyard's formula for continuous diffusion [14]

$$\Delta E = 2\hbar\kappa^2 D \quad (7)$$

if for D the macroscopic diffusion constants for both models [15] are inserted ($D_{t-t} = a^2/48\tau$; $D_{o-o} = a^2/24\tau$).

The formalism described so far neglects the

oscillatory part of $G_s(r, t)$ which is superimposed on the diffusive motion. This oscillatory motion manifests itself in the inelastic scattering caused by lattice modes and by the localized modes of the hydrogen. Furthermore, the intensity of the quasielastic line according to equation (4) should be multiplied by a Debye-Waller factor, and by a Bessel function J_0 [16, 17] which takes into account the existence of localized modes.

3. EXPERIMENTS AND RESULTS

The experiments were performed with the rotating crystal spectrometer at the I-RJ-2 (Dido) reactor[18] with an incident energy of $4.8 \cdot 10^{-3}$ eV. The resolution width was $2.7 \cdot 10^{-4}$ eV (full width at half maximum) at this energy. Four scattering angles θ were measured simultaneously. The resolution functions at different θ were determined with the sample at such a temperature ($\sim 100^\circ\text{K}$) at which ΔE is negligible. They were found to be close to Gaussian functions of the energy.

The sample consisted of approximately 250 niobium rods of 0.12 cm dia. and 10 cm length. Starting material was zone refined niobium (MRC) which was outgassed at 10^{-9} – 10^{-10} Torr. at 2200°C . After this procedure the residual resistivity ratio was better than 1000. Loading was performed at 500°C from the gas phase with purified hydrogen. The hydrogen content was determined from the weight increase. Samples with 3.2 and 33 at.% (approximately the critical concentration) were prepared. Before the measurements the loaded samples were annealed in the scattering thermostat for 24 hr at 308°C to homogenize the sample. Inspection by X-ray diffraction showed that the rods had a non-ideal polycrystalline structure; the [110]-axis of the grains was predominantly oriented parallel to the rod axis. The critical temperature of our sample ($T_c = 149^\circ\text{C}$) is appreciably lower than the values published in the literature [1, 19, 20].

Figure 4 shows typical time-of-flight spec-

tra. The peak at $4.8 \cdot 10^{-3}$ eV is the quasi-elastic line, followed by the inelastic spectrum due to the lattice vibrations, and the pronounced modes in the region of 0.1–0.2 eV, consistent with the values reported by Verdan *et al.*[4]. The width of these peaks is due to the resolution and due to multiphonon processes. A further contribution might come from the interaction of the hydrogen oscillators, which are, therefore, no more strictly localized. The natural width of these modes, which has been discussed in connection with a band model of protons[4] can only be determined by scattering experiments at very small κ .

The spectra in Fig. 4 were corrected for background, which in contrast to liquids was small below the quasi elastic line. The room background was determined from the intensity between the pulses at sufficiently large flight times where the intensity scattered from the protons is negligible. The background from the host lattice and from the sample container was determined from an unloaded sample. The transmission as estimated from the bound cross section σ_{inc} was 87 per cent.

In Fig. 5 corrected experimental curves are compared with calculated curves as determined by folding the measured resolution curve with equation (4) by suitably adjusting the width ΔE of the Lorentzian in equation (4). A good fit is achieved in spite of the fact that the scattering law is a sum of Lorentzians. It has been checked that a correction due to the interrelation of momentum and energy transfer at a given scattering angle is not necessary. For most of the curves ΔE has been determined by a procedure described by Melkonian[21]. In this procedure one makes use of diagrams which interconnect the halfwidth of a Lorentzian, the halfwidth of a Lorentzian folded with a Gaussian, and the width of a Gaussian. The validity of this procedure was demonstrated for the curves in Fig. 5 and was found to give consistency.

In Fig. 6 the halfwidths as determined are plotted for six representative temperatures as

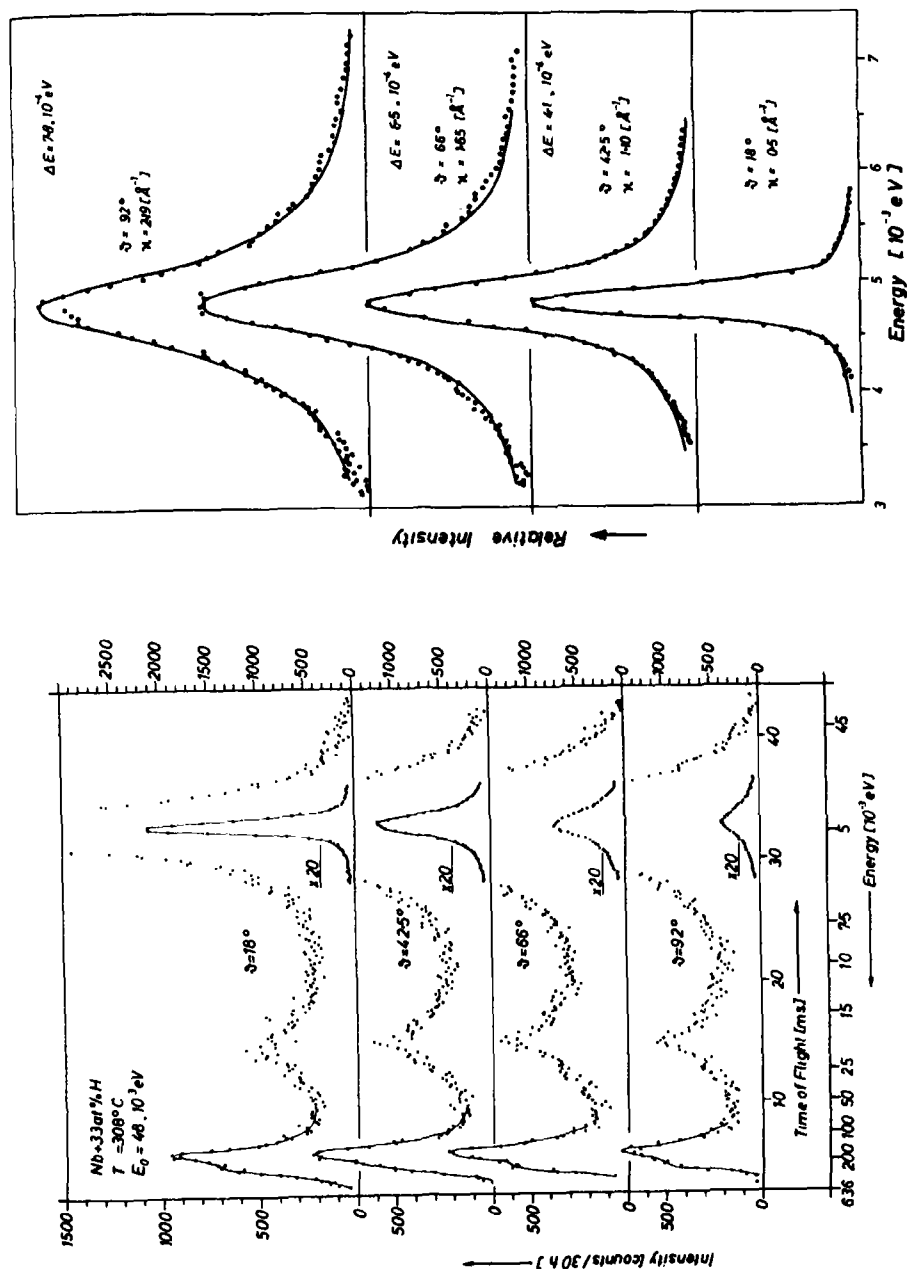


Fig. 4. Typical time-of-flight spectra. The quasielastic peak is centered at the incoming energy, $E_0 = 0.0048$ eV. The peaks at 0.1–0.2 eV are due to the localized modes of H in Nb; the structure centered at about 0.02 eV results from the host lattice vibrations, into which the protons are embedded ($\theta =$ scattering angle).

Relative Intensity

Energy [10^{-3} eV]

Fig. 5. Four typical quasielastic lines at 308°C. The dots are experimental results. The solid curve is calculated by folding a simple Lorentzian of the half width ΔE with the experimental resolution function. The lowest curve is practically identical with the resolution function.

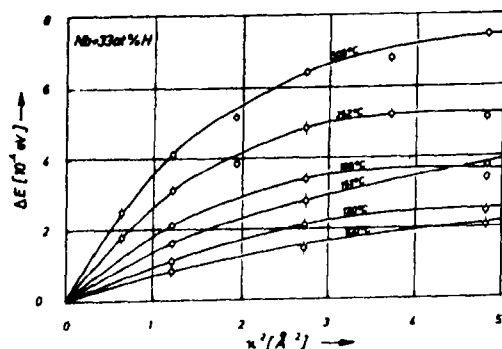


Fig. 6. Representative results of the half width ΔE of the quasi-elastic line

a function of κ . The error bars indicate statistical errors only. The curves show qualitatively

the behaviour as discussed in Section 2. The deviation from the linear part at small κ occurs around $\kappa^2 = 1 \text{ \AA}^{-2}$ in contrast to $\kappa^2 = 3 \text{ \AA}^{-2}$ in the measurements of Verdan *et al.*[4]. This discrepancy can hardly be attributed to the different hydrogen concentration since analogous curves as in Fig. 6 have been found for 3.2 at.% hydrogen, a concentration smaller than that used by Verdan *et al.* (9 per cent). Although the highest κ -value in our experiments is about the same as that used by Sköld and Nelin[3], a maximum in ΔE vs. κ^2 was not observed. This can be attributed to the fact that the first reciprocal lattice vector of the interstitial lattice has a smaller value in the case of palladium than in the case of niobium.

Figure 7 summarizes the available data for the measurements at the critical concentration

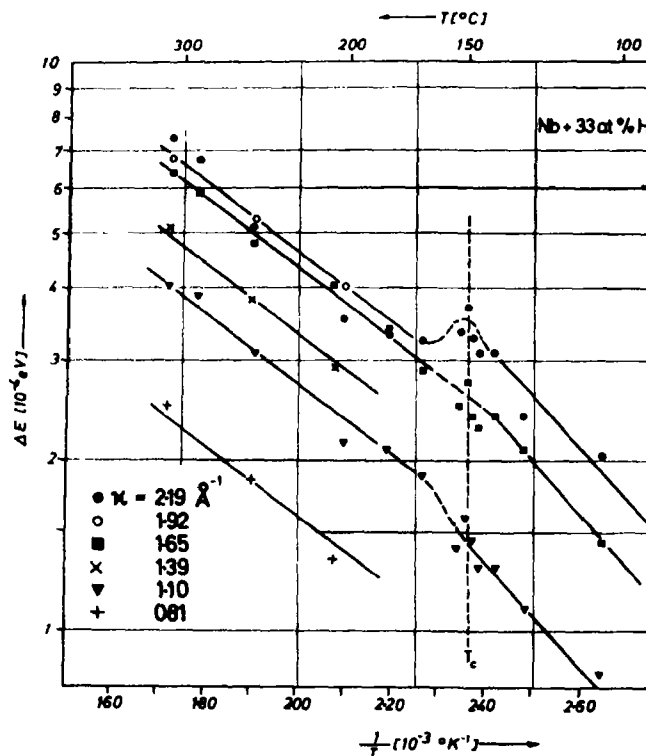


Fig. 7. Arrhenius plot of the half width ΔE for different κ -values.

(33 per cent) in a plot of ΔE against $1/T$ with κ as a parameter (Arrhenius plot). Within the limits of error, the experimental points can be connected by straight lines. An anomaly is observable at temperatures close to T_c for large scattering vectors κ .

For 3.2 per cent, measurements at only two temperatures were performed (see Table 1).

Assuming a Debye-Waller factor of the form $e^{-\kappa^2 u^2}$ the mean square oscillatory amplitude u^2 was extracted from a plot of the logarithm of the area of the quasi-elastic peak against κ^2 . For 308°C u^2 was found as approximately $0.18 \text{ \AA}^2$, compared to $0.13 \text{ \AA}^2$ for H in Pd[3]. Furthermore, a drastic change of the relative peak intensities at different κ was found, starting in the region of the critical temperature (Fig. 8). Since the relative change of the width of the quasielastic line in passing the critical point is small, the step in Fig. 8 can be considered representative for the relative change in the Debye-Waller factor. The corresponding change in u^2 between 170° and 130°C amounts to $\Delta u^2 = 0.07 \text{ \AA}^2$ which is 40 per cent of the value at 308°C. Within the experimental accuracy of these data they will not essentially be influenced by taking into account the Bessel function factor mentioned in Section 2, assuming purely localized modes.

4. DISCUSSION

For small κ -values ($\leq 1.1 \text{ \AA}^{-1}$) the diffusion constant was determined by means of equation (7). Table 1 presents our results for three temperatures and two concentrations. The errors are estimated; they are mainly due to

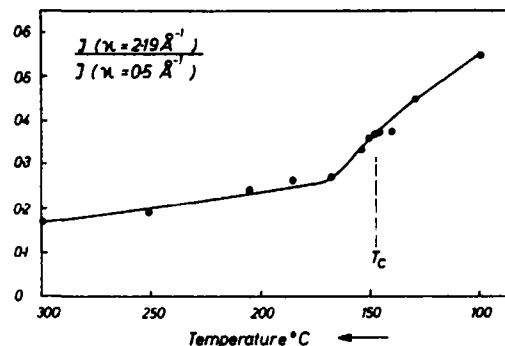


Fig. 8. Ratio of the peak intensity of the quasielastic line at $\kappa = 2.19 \text{ \AA}^{-1}$ and $\kappa = 0.5 \text{ \AA}^{-1}$.

multiple scattering and to the resolution correction. The results of Verdan *et al.*[4] and Schaumann *et al.*[11] are included. The diffusion constant is as high as in real liquids (see e.g.[22]). Our measurements at low concentration show good agreement with results by the relaxation method[11]. In both experiments samples with identical purification and preparation procedure have been used. The agreement of the results of the two completely independent methods emphasizes the reliability of the data. Table 1 shows that the diffusion constant of the low and the high concentration samples differs only by a factor of about 2. A decrease of D with increasing concentration is consistent with observations on palladium[3, 23].

Figure 7 shows that the temperature dependence of ΔE above the critical temperature T_c does not depend on κ , consistent with the model of a simple diffusion process where ΔE is proportional to $1/\tau$ for all κ values. From the slope an activation energy was found which is $U = 0.12 \text{ eV}$ for 33 per cent compared to

Table 1. Diffusion constant D (cm^2/sec) for protons in Nb

	Neutron scattering [4]	Neutron scattering, this work	Relaxation method [11]
Concentration (at.%)	9%	33%	3.2%
$T = 120^\circ\text{C}$	—	$0.8 \cdot 10^{-5}$	$(2.0 \pm 0.2) \cdot 10^{-5}$
$T = 210^\circ\text{C}$	$2 \cdot 10^{-5} (200^\circ\text{C})$	$1.6 \cdot 10^{-5}$	$(3.5 \pm 0.3) \cdot 10^{-5}$
$T = 310^\circ\text{C}$	—	$2.7 \cdot 10^{-5}$	—
			$(6.0 \pm 0.2) \cdot 10^{-5}$

0.11 eV for low concentration[11]. With $D = D_0 e^{-U/kT}$ one finds $D_0 = 3.3 \cdot 10^{-4}$ cm²/sec for 33 per cent compared to $5.5 \cdot 10^{-4}$ for low concentration[11]. By NMR measurements the correlation time $1/\nu = 1/\nu_0 e^{U/kT}$ for protons in niobium with 70 per cent hydrogen has been studied[8], yielding the following results: $U = 0.160$ eV and $1/\nu = 5 \cdot 10^{-13}$ sec.

Besides the diffusion coefficient D , the mean time of stay τ can be extracted from the κ -dependence of the half width (Fig. 6). The relation between D and τ is model dependent (see equation 8 below). Therefore in principle, a decision between different jump models is made possible by discussing the following theoretical quantity:

$$\frac{\Delta E (\kappa = 2.2 \text{ \AA}^{-1})}{(\Delta E / \kappa^2 a^2)_{\kappa \rightarrow 0}} = \begin{cases} 30 & (26) & (t-t) \\ 20 & (18) & (o-o) \end{cases} \quad (8)$$

The first numbers refer to the $(t-t)$ and $(o-o)$ model in an ideal polycrystal, whereas the numbers in brackets correspond to the $[110]$ texture as described in section 3. ΔE at $2.2 \text{ \AA}^{-1}$, which is the highest experimental κ -value, has been taken from the calculated curves in Fig. 3. For $\Delta E / \kappa^2 a^2$, the equations (6) have been inserted in equation (8). In Fig. 9 the experimental results for the ratio of equation (8) are plotted versus temperature together with the calculated numbers. Above T_c the results are in favour of the octahedral model. Below T_c the ratio of equation (8) is close to that of the tetrahedral model. This observation would mean, that the condensation is accompanied with a change in the type of the preferred positions of the protons. Yet this conclusion must be considered with great caution since below T_c the interpretation of the data is not completely unambiguous due to the existence of two phases which both contribute to the observed quasielastic width.

Using the octahedral model the mean time of stay at 308°C is about $\tau = 2 \cdot 10^{-12}$ sec. This value is comparable with the shortest mean time of stay in real liquids. A final remark con-

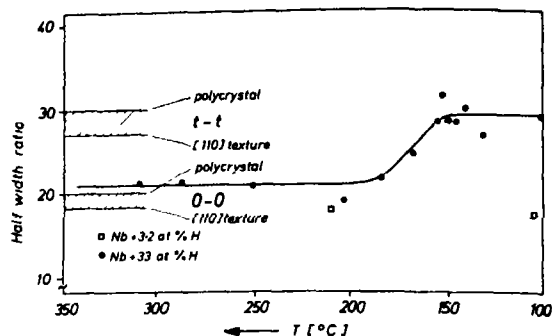


Fig. 9. Halfwidth ratio according to equation (8). The theoretical values for $(o-o)$ and $(t-t)$ jumps are indicated.

cerns the Debye-Waller factor. The mean square displacement $u^2 = 0.18 \text{ \AA}^2$ at 308°C is unusually large for a solid. For protons e.g. in ice one finds $u^2 \approx 0.07 \text{ \AA}^2$. This latter value is being approached below the critical point. The reason for the large Debye-Waller factor above T_c and for the drastic change in passing T_c remains open to discussion because there was no observable change in the localized modes nor in the lattice modes which could account for such a large change. Further scattering experiments, especially close to T_c , are under way.

Acknowledgements—The authors are greatly indebted to Dr. F. Hößfeld for his valuable help in performing the computer calculations, and Dr. Cocking, Harwell, for critically reading the manuscript.

REFERENCES

1. WALTER R. J. and CHANDLER W. T., *Trans. AIME* **233**, 762 (1965).
2. ALEFELD G., *Phys. Status Solidi* **32**, 67 (1969).
3. SKÖLD K. and NELIN G., *J. Phys. Chem. Solids* **28**, 2369 (1967).
4. VERDAN G., RUBIN R., KLEY W., *Proc. IAEA Symp. Neutron Inelastic Scattering*, Vol. 1, p.223. Vienna (1968); For a review on hydrogen in metals see: PAN S. S., YEATER M. L. and MOORE W. E., *Proc. Symp. Molecular Dynamics and Structure of Solids*, Washington, NBS-301, p. 315 (1969).
5. STOCKMEYER R. and STILLER H., *Phys. Status Solidi* **27**, 269 (1968).
6. CHUDLEY C. T. and ELLIOTT R. J., *Proc. Phys. Soc.* **77**, 353 (1960).
7. BLAESSER G. and PERRETTI J., *Proc. int. Conf. Vacancies and Interstitials in Metals*, KFA Jülich, JÜL-Conf.-2, Vol. 2, p. 886 (1968).

8. ZAMIR D. and COTZ R. M., *Phys. Rev.* **134A**, 666 (1964).
9. CANNELLI G. and VERDINI L., *Ric. Sci.* **36**, 98 (1966).
10. SCHILLER P. and SCHNEIDER A., *Proc. int. Conf. Vacancies and Interstitials in Metals*, KFA Jülich, JÜL-Conf.-2, Vol. 2, p. 871 (1968).
11. SCHAUMANN G., VÖLKL J., ALEFELD G., *Phys. Rev. Lett.* **21**, 891 (1968).
12. VAN HOVE L., *Phys. Rev.* **95**, 249 (1954).
13. GISSLER W. and RÖTHER H., To be published.
14. VINEYARD G. H., *Phys. Rev.* **110**, 999 (1954).
15. CONDIT H. and BESHES D. N., *Trans. AIME* **239**, 680 (1967).
16. KAUFMAN B. and LIPKIN H. J., *Ann. Phys.* **18**, 294 (1962).
17. KRIVOGLAZ M. A., *Soviet Phys. JETP* **19**, 432 (1964).
18. AXMANN A. and GISSLER W., Report JÜL-338-NP (1965).
19. ALBRECHT W. M., GOODE W. D. and MALLET M. W., *J. Electrochem. Soc.* **106**, 981 (1959).
20. VELECKIS E., Thesis, Illinois Institute of Technology (1960).
21. MLEKONIAN E., *Proc. Int. Conf. Peaceful Uses of Atomic Energy*, Vol. 4, p. 340. United Nations, New York (1956).
22. LARSSON K. E., *Proc. IAEA Symp. Neutron Inelastic Scattering*, Vol. I, p. 397, Vienna (1968).
23. ARONS R. R., *Proc. Int. Conf. Vacancies and Interstitials in Metals*, KFA Jülich, JÜL-Conf.-2, Vol. 2, p. 901 (1968).

TECHNICAL NOTES

Disorder in the normal paraffin from $8 \leq n \leq 16$

(Received 6 November 1969;

in revised form 16 March 1970)

IF THE specific heat of a substance rises more rapidly than would be expected in the temperature region below either a transition or fusion temperature then it is probable that two states of differing energies coexist. Physically the nature of these two states can be quite different for different substances even though the specific heat behavior may be qualitatively quite similar. Thus, for example, the randomization of atomic species which occurs in alloys such as β brass with increasing temperature led to the concept of two states, one completely ordered as regards atomic positions, and one completely disordered. For this case, furthermore, the energy barrier between the two states is dependent on the extent to which disorder has replaced order, so that one may speak of a cooperative transition. An analogous situation exists in silver halides where lattice defects, in the form of holes and interstitial Ag^+ ions, are formed with increasing temperature. In these cases transport of atoms takes place to either other lattice positions or to interstitial positions. The concepts of order disorder and of defect structure can be usefully applied in other contexts. In the low-high temperature transformation of quartz, for example, only small movements of atoms are involved which result in a change in crystal structure. It is possible to successfully analyze the specific heat and thermal expansion and contraction of quartz in terms of a defect model in which the high-temperature structure is considered, on a local scale, as an imperfec-

tion in a low-temperature lattice[1]. Discussions of disorder, primarily rotational in nature, in paraffin hydrocarbons have tended to deal with those chains with $n > 18$ since these are most accessible to measurements [see, for example, the discussion by Daniel [2]]. The specific heats of the normal paraffins for $8 \leq n \leq 16$ [3] indicate that disorder may exist in these hydrocarbons as well, and it is of interest to see whether the thermal data can be interpreted in these terms. The specific heats reflect the energy needed to change the state of a system, and are thus gross in the sense of the physical model, since, conceivably, different models, all of which require energy for a change of state, may lead to similar results. We nevertheless proceed on the basis that a particular model is likely to be correct if the functional form of the result predicted by the model is verified by experiment, particularly if, as is true for the hydrocarbons, other molecules in a sequence are known to exhibit behavior characteristics of this model. The model to be used is a simple two-state model, and this note is limited to the question of the adequacy of this model for the interpretation of the thermal data. No attempt is made to define in detail the physical features of the model since this would require additional data using other types of measurement and a considerably more extensive discussion. The results are nevertheless of interest in defining the chain lengths at which order-disorder effects become significant and in relating these to a diverse set of phenomena in other substances which can be treated by a simple two-state model.

Briefly stated, the treatment is as follows. The fraction of imperfections, n/N , is, in

general, given by an expression of the type

$$n/N = A \exp \{W(s)/RT\} \quad (1)$$

where A is a constant dependent on the configurational degeneracy of the two states, $W(s)$ is the energy barrier with s , an order parameter, being a function of the temperature, R is the gas constant, and T the temperature. Over the range of temperatures of interest here, the number of imperfections is small and $W(s)$ is essentially constant and equal to W_0 , i.e., the imperfections are essentially isolated and independent of each other. This results then in the equation

$$\log (T^2 \Delta c_p) = \log \frac{AW_0^2}{R} - \frac{W_0}{RT} \quad (2)$$

where Δc_p is the excess specific heat due to the formation of imperfections. The result is well suited to a straightforward and simple determination of the potential barrier, W_0 , from the straight line plot of $\log (T^2 \Delta c_p)$ vs. $1/T$.

The specific heat data of Finke *et al.*[3] were used. The excess specific heat was obtained by graphical extrapolation of the lower temperature data as the normal specific heat and subtraction of this from the measured total value, and this was then used for the

straight line plot indicated by equation (2). The resulting values of W_0 are listed in Table 1. The calculated barriers are undoubtedly less reliable for the smaller chain lengths because of the greater difficulty in the estimation of the excess specific heat.

The fraction of defects for a temperature ten degrees below either the fusion or transition temperature has been calculated from equation (1) and is also included in Table 1. The temperature has been chosen, arbitrarily, in order to provide some comparability of conditions. The fraction of defects at the fusion or transition temperature has been estimated from the extrapolation of $T^2 \Delta c_p$ curves and is also listed in Table 1. These have also been plotted in Fig. 1.

The excess entropy due to defect formation can be calculated in the following way. The excess entropy is given by

$$\Delta S = \int (\Delta c_p/T) dT = \int_{T_0}^T (W/T) \frac{d(Ae^{-W/RT})}{dT} \quad (3)$$

Integrating by parts, and choosing T_0 sufficiently low so that n/N is zero, we have

$$\Delta S_T = \left(\frac{W}{T} + R \right) \left(\frac{n}{N} \right)_T \quad (4)$$

where the subscript T indicates the tempera-

Table 1. Energy barrier and fraction of defects determined from the excess specific heat for the normal paraffins for $8 \leq n \leq 16$

n	W_0 , kcal/mol	n/N - % (T_f or T_t)-10°	n/N - % T_f or T_t
8	4.8	0.7	1.1
9	5.3	0.9	2.0
10	5.7	1.1	1.7
11	4.3	2.4	3.2
12	4.4	5.1	7.7
13	4.7	5.2	9.3
14	4.4	7.8	11.7
15	5.0	6.7	12.5
16	4.6	9.6	12.8

T_f = fusion temperature T_t = transition temperature

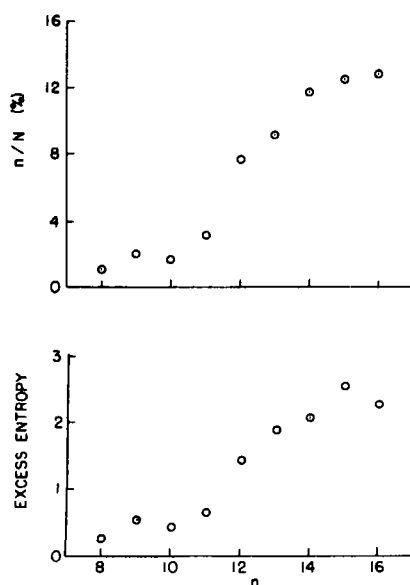


Fig. 1.

ture up to which the excess entropy is being calculated. The excess entropy calculated up to the fusion temperature for the even numbered hydrocarbons is given in Table 2 and plotted in Fig. 1. The sum of these and the entropy of fusion and, where applicable, the entropy of transition is also given in Table 2. The entropy sum has been plotted in Fig. 2. The entropies of fusion and transition have been taken from Finke *et al.*[3].

Table 2. Excess and total entropies for $8 \leq n \leq 16$

n	Entropy of fusion	Entropy of transition	Excess entropy	Total entropy
8	22.9	—	0.26	23.2
9	16.83	6.91	0.52	24.26
10	28.18	—	0.42	28.60
11	21.41	6.93	0.64	28.98
12	33.40	—	1.43	34.83
13	25.44	7.18	1.89	34.51
14	38.61	—	2.07	40.68
15	29.20	8.09	2.56	39.85
16	43.77	—	2.28	46.05

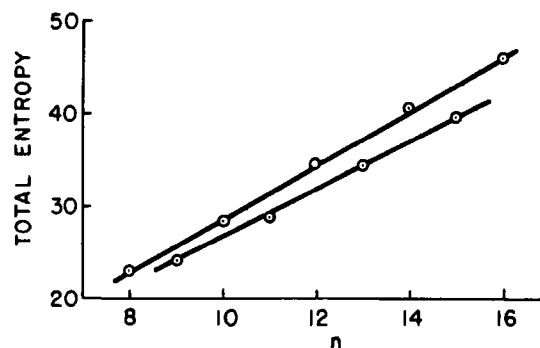


Fig. 2.

DISCUSSION

The specific heats of the normal paraffins for $8 \leq n \leq 16$ can be treated in terms of order-disorder by the use of equations (1) and (2). The resulting energy barriers are of the same order of magnitude as are found for the larger chain hydrocarbons for which the phenomenon is better developed. No systematic trend is found over the range from $8 \leq n \leq 16$. The fraction of defects, however, is low for $8 \leq n \leq 11$ compared to those for $12 \leq n \leq 16$ when calculated either at ten degrees below the fusion or transition temperatures or at these temperatures themselves. Hence we may conclude that significant order-disorder effects become increasingly evident for $n \geq 12$. This appears also to be reflected in the calorimetrically determined entropies of transition. A similar effect, as would be expected, is shown by the excess entropy resulting from the formation of the defects, with significant contributions to the total entropy occurring for $n \geq 12$. Finally, the total entropy, taken as the sum of the entropies of fusion, transition and defect formation, can be well represented by two straight lines for the even and odd series, respectively.

S. M. SILVERMAN

Air Force Cambridge Research Laboratories,
Laurence G. Hanscom Field,
Bedford, Mass. 01730 U.S.A.

REFERENCES

1. SILVERMAN S. M., *J. chem. Phys.* **25**, 1081 (1956).
J. Geophys. Res. **75** in press. (1970).
2. DANIEL V., *Adv. Phys. (Phil. Mag. Suppl.)* **2** 450 (1953).
3. FINKE H. L., GROSS M. E., WADDINGTON G. and HUFFMAN H. M., *J. Amer. Chem. Soc.* **76**, 333 (1954).

J. Phys. Chem. Solids Vol 31, pp 2374-2377

Thermopower of cubic transition metals*

(Received 4 February 1970)

WE HAVE measured the thermopower of the transition metals vanadium, niobium, tantalum, molybdenum, tungsten, rhenium, rhodium, and iridium. The measurements were performed on wires of 99.99 per cent purity supplied by Materials Research Corporation; using an apparatus similar to that of Henry and Schroeder[1]. Except for rhenium which has a hexagonal close packed structure these metals are cubic and the single component of the thermopower tensor can therefore be measured on polycrystalline wires. For rhenium the results will be some kind of average over the two components of the thermopower tensor which applies to hcp metals. The main object is to compare the results for the three groupings (V, Nb, Ta), (Mo, W), (Rh, Ir), within which the elements have similar outer shells of electrons.

In Figs. 1-4 we show the thermopowers of the metals in the above groupings. The results for Va are similar to those of Potter[2] and McIntosh and Sill[3], except that we did not observe the small anomaly seen by them at 217°K. The Nb results agree with those of Weinberg and Schultz[4] and Potter[2], but join rather crudely to the high temperature data of Raag and Kowger[5]. Our low

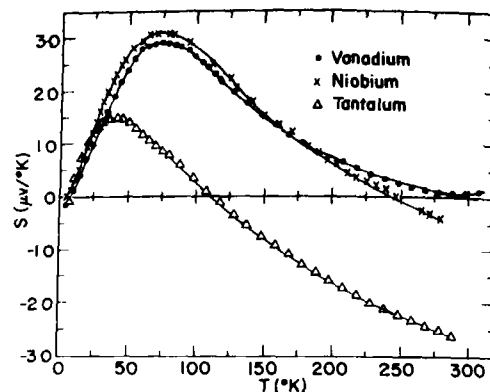


Fig. 1. Thermopower of vanadium, niobium, and tantalum.

temperature results for Mo and W join neatly onto the results calculated from Lander's [6] high temperature Thomson coefficient measurements and also, for W, onto the results of Raag and Kowger[5]. For W, the thermopower becomes positive at the lowest temperature in agreement with Trodahl[7]. Measurements on tungsten wire drawn from a zone refined sample gave results $\sim 0.02 \mu\text{V}/^\circ\text{K}$ less than the M.R.C. tungsten for temperatures greater than 40°K. Our rhodium and iridium results differ markedly from those of Potter[2].

The most striking feature of the results is the similarity of the results for the metals within each of the above groupings. Undoubtedly this is related to the similarity of the Fermi surfaces within each grouping. We now briefly consider ways in which the Fermi surface properties may manifest themselves. First of all we assume that the low temperature peaks occurring in the vicinity of $\theta_D/5$, where θ_D is the Debye temperature, are caused by phonon drag. The simplest picture to explain the sign of these peaks appears to apply remarkably well to Mg, Zn and Cd[8]. In Fig. 5(a), we show a phonon induced transition between two states on an electron sheet of the Fermi surface in the periodically extended zone scheme. For such a transition the electron velocity v in the direction of the

*This work was supported by the National Science Foundation.

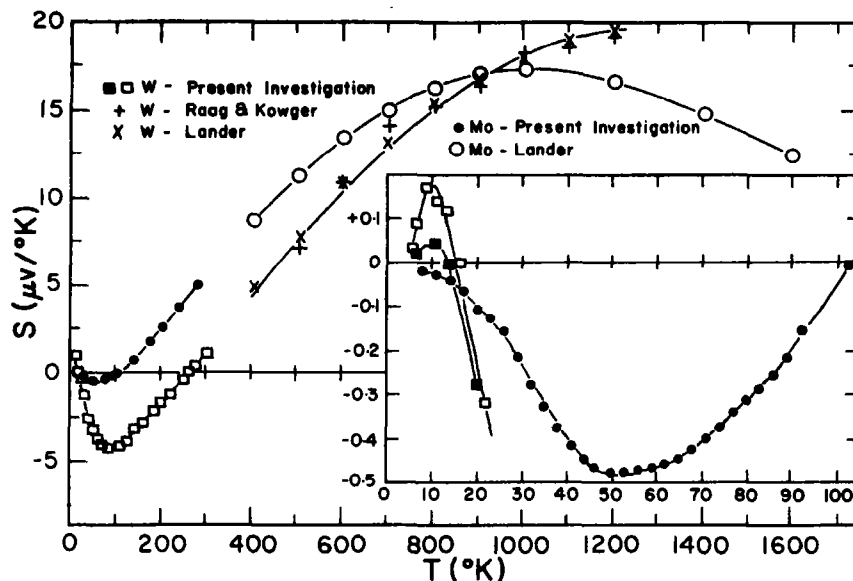


Fig. 2. Thermopower of molybdenum and tungsten. ■—zone refined tungsten; □—99.99% purity tungsten.

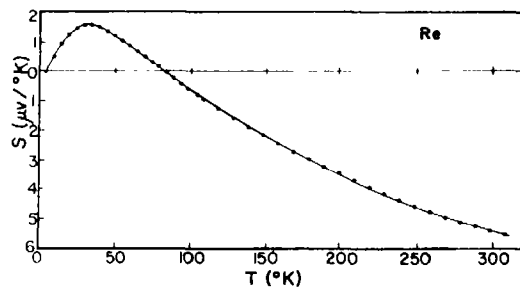


Fig. 3. Thermopower of rhenium.

phonon wave vector is increased. This leads to a negative contribution to the phonon-drag thermopower[9, 10]. Conversely, the transition across the hole region of the Fermi surface illustrated in Fig. 5(b) leads to a positive contribution to the thermopower. Transitions like that labelled q' in Fig. 5 lead to a smaller contribution than q because only a component of the electron velocity is reversed. At the lowest temperature we expect the sign of the phonon drag thermopower to be determined by the nature, hole or

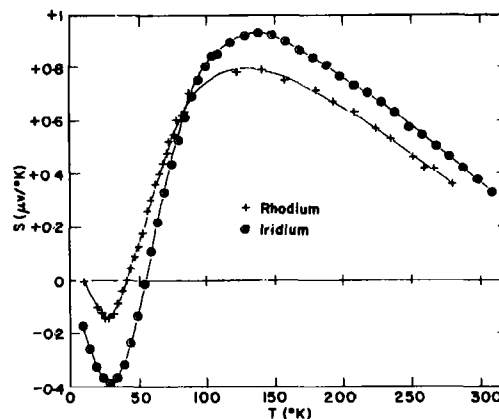


Fig. 4. Thermopower of rhodium and iridium.

electron, of the piece of Fermi surface with the smallest calliper dimensions. There will be relatively few phonons with wave vector large enough to span the larger surfaces. As the temperature increases we expect the contribution of the next largest piece of Fermi surface to begin to predominate. In the vicinity of $\theta_D/5$ the phonon drag thermopower

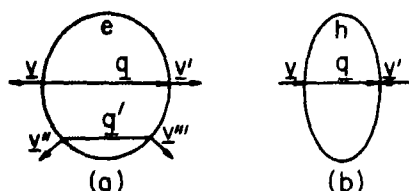


Fig. 5. Phonon induced transitions across the Fermi surface

usually begins to decrease because of phonon-phonon scattering.

This highly simplified picture would lead us to expect the observed positive phonon drag thermopower in the vanadium group of metals since the proposed Fermi surface of these metals is made up of hole sheets [11, 12].

For W and Mo the situation is complicated by the presence of hole and electron sheets [11, 13, 14]. For W the smallest pieces of Fermi surface are hole sheets (at N in Ref. [13]) with dimensions significantly smaller than the next largest surface which is an electron sheet. This may account for the initial positive thermopower in tungsten and the large negative dip thereafter. In Mo analogous pieces of Fermi surface are much closer to being equal. Furthermore Mo has an additional small electron sheet (the lenses of Ref. [13]). It would appear that contributions from these sheets tend to cancel and produce a comparatively small negative contribution only in Mo.

In rhenium the three smallest sheets of the Fermi surface are hole sheets [15]. We therefore expect the observed positive contribution to the phonon drag thermopower.

When we come to Rh and Ir the above picture does not fit at all. The smallest pieces of Fermi surface are hole sheets and these are significantly smaller than the electron sheets [16, 17]. To make any sense of these results we have to resort to the possibility of interband transitions using arguments similar to those used by Fletcher and Greig [18] to explain the positive phonon drag peaks in palladium and platinum. So far we have

ignored interband transitions, in part because the q vectors associated with these tend to be large in the first two groups of metals considered above, and in part, because frequently any such transition which does occur would be expected to make a comparatively small contribution to the thermopower, since the electron velocity is not reversed as it is in the situations illustrated in Fig. 4. For Rh and Ir the situation is rather like that in Pt and Pa. The q vector connecting different bands in certain directions becomes much smaller than the dimensions of the Fermi surface sheets themselves. Furthermore such transitions are augmented by the high density of states associated with the d -like character of the wave functions over the sheet of the Fermi surface in the second zone. It now becomes even more difficult to predict the sign of the thermopower. At best we can say that the experimental results strongly suggest the importance of interband transitions in Rh and Ir so far as the thermopower is concerned.

Finally we note that Colquitt and Fankhauser [19] have performed a detailed study of the effects of phonon induced and electron-electron interband s - d transitions. They point out that both the small positive peak observed in W at $T < 12^\circ\text{K}$ and the results for W and Mo above the Debye temperature could be caused by electron-electron interband scattering.

Department of Physics,
Michigan State University,
East Lansing,
Mich. 48823, U.S.A.

R. CARTER
A. DAVIDSON
P. A. SCHROEDER

REFERENCES

1. HENRY W. G. and SCHROEDER P. A., *Can. J. Phys.* **41**, 1076 (1963).
2. PÖTTER H. H., *Proc. phys. Soc. Lond.* **53**, 695, (1941).
3. McINTOSH A. R. and SILL L., *J. Phys. Chem. Solids* **24**, 501 (1963).
4. WEINBERG J. and SCHULTZ C. W., *J. Phys. Chem. Solids* **27**, 474 (1965).
5. RAAG V. and KOWGER H. V., *J. appl. Phys.* **36**, 2045 (1965).
6. LANDER J. J., *Phys. Rev.* **74**, 479 (1948).
7. TRODAHL H., *R.S.I.*, **40**, 648 (1969).

8. ROWE V. A. and SCHROEDER P. A., *J. Phys. Chem. Solids* **31**, 1 (1970).
9. ZIMAN J. M., *Adv. Phys.* **10**, 1 (1961).
10. BAILYN M., *Phys. Rev.* **120**, 381 (1960).
11. MATTHEISS L. F., *Phys. Rev.* **139**, A1893 (1965).
12. FAWCETT E., REED W. A. and SODEN R. R., *Phys. Rev.* **159**, 533 (1967).
13. SPARLIN D. M. and MARCUS J. A., *Phys. Rev.* **144**, 484 (1966).
14. LOUCKS T. L., *Phys. Rev.* **143**, 506 (1966).
15. MATTHEISS L. F., *Phys. Rev.* **151**, 450 (1966).
16. COLERIDGE P. T., *Proc. R. Soc.*, **A295**, 476 (1966).
17. ANDERSON O. K. and MACKINTOSH A. R., *Solid State Commun.* **6**, 285 (1968).
18. FLETCHER R. and GREIG D., *Phil. Mag.* **17**, 21 (1968).
19. COLQUITT C. L. and FANKHAUSER H. R., (To be published).

HIGH FIELD BEHAVIOUR OF ZnO-I INVESTIGATION OF THE DARK CURRENT

H. KIESS

Laboratories RCA, Ltd., Zurich, Switzerland

(Received 29 December 1969; in revised form 18 February 1970)

Abstract—The dark I-V-characteristics of conducting ZnO single crystals in contact with electrolytes were investigated. Under positive bias a sharp rise of current occurs at a threshold voltage of about 5 V. A quantitative analysis of the I-V-characteristic shows, that tunnelling of charge carriers occurs from a surface state which is situated about 0.6 eV below the conduction band edge. As the results are not influenced by the choice of the electrolyte, it is felt that this surface state is a property of the ZnO used for the investigations. No carrier multiplication could be observed with these crystals even at fields as high as $1.6 \cdot 10^6$ V/cm.

1. INTRODUCTION

NUMEROUS publications on the ZnO-electrolyte interface have appeared since the classical work of Dewald[1] studying current and capacitance as a function of voltage. A common factor to all these investigations[2-4] is that only low voltages are applied so that quasi-equilibrium exists between the surface and the bulk of the crystal. For such a case the carrier concentration at the surface and the current flowing through the interface were calculated by Dewald. He showed that at 'high' anode voltages—but still in the regime of quasi-equilibrium—a saturated current is to be expected. Above a certain threshold voltage the assumptions made for this calculation are no longer valid and the question arises whether the increase in current is due to injection of majority carriers or generation of charge carriers by impact ionization.

In a more recent paper Williams and Willis [5] reported on capacitance and current measurements on ZnO single crystals in contact with electrolytes under positive bias up to 100 V. Obviously quasi-equilibrium can no longer be assumed to exist and indeed, Williams observed a strong increase of the current at high voltages. He concluded that impact ionization across the band gap occurs causing carrier multiplication. In the paper

presented here a more detailed investigation of this high voltage behaviour of ZnO in contact with electrolytes is given. The experiments show that the I-V-characteristic has a complicated structure which is rather insensitive to the composition of the electrolyte, which indicates that solid state effects dominate. It is shown that the strong current increase is due to tunneling of charge carriers from surface states at the ZnO-electrolyte interface situated at about 0.6 eV below the conduction band-edge. It was found that in the high voltage region in all the investigated conducting ZnO crystals a Schottky-barrier is formed near the surface, though complications arise due to the existence of two types of donors. Evaluation of our measurements gave a concentration of deep donors of about $8 \cdot 10^{17} \text{ cm}^{-3}$, and a concentration of shallow donors (probably ionized Zn) of about $2 \cdot 10^{16} \text{ cm}^{-3}$.

2. EXPERIMENTAL TECHNIQUE

Two ZnO single crystals from different batches were obtained from the 3-M company. The crystals were *n*-type conducting and the resistivity was in the order of $1.0 \Omega \text{ cm}$. They were cut into discs of about 1-2 mm in thickness, with the hexagonal *c*-axis perpendicular to the broad face. The diameter of the discs was about 4-5 mm. Before the measurement

the surfaces were polished and etched for a short time with 85 per cent phosphoric acid.

The crystals were provided with an ohmic contact on one of the broad faces. Since the values of the electrode potentials were high and the current mostly low, it was necessary to provide good insulation. The most convenient material was found to be black wax applied to the sample so as to leave portion of the face exposed to the electrolyte. This raises the question of the purity of the electrolyte. Probably it was contaminated, but since the major part of the observations involved the solid phase, the conclusions drawn from the experiments should not be too seriously influenced. An acidic, neutral, or basic buffered 2 M KCl solution was used as the electrolyte. If not otherwise stated the results discussed here refer to measurements with acetate buffered 2 M KCl solution of $p_H \sim 4.5$. A schematic diagram of the crystal mounting and the circuit for current and charge measurements is shown in Fig. 1. The voltage was applied between the sample and a platinum electrode dipped into the electrolyte, the electrolyte contact being negative in all cases. A Keithley-electrometer 601 was used to measure the direct current, whereas the charge and the transient currents flowing under pulsed conditions were determined with an operational amplifier the output of which was displayed on a Tektronix oscilloscope 545 B.

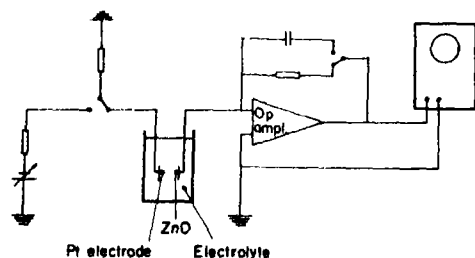


Fig. 1. Schematic diagram of the measuring circuit. Switch S_1 , a mercury relay, was used to switch on and off the voltage. Current measurements were made with the resistor in the feedback loop and charge measurements with the capacitor.

The capacitance was either calculated from the charge and the applied voltage or determined from the time constant of the transient currents. In addition the differential capacitance under dc bias was also measured with a Wayne-Kerr Universal Bridge B221.

Conductivity and Hall effect were measured as a function of temperature in order to determine the ionization energy and impurity concentrations.

3. RESULTS

(a) I-V-Characteristic and photocurrent

Figure 2 shows the dark current as a function of the positive bias voltage. The dark current at low voltages (in acidic or basic solution) is due to the dissolving of the crystal in the electrolyte[2]. In the voltage range between 4–15 V a sharp increase of the current over several orders of magnitude is observed. The curve flattens off above 20 V and a nearly voltage independent current flows in the voltage regime between 20–40 V. Above 40 V the current rises sharply and above 100 V it reaches values at which the ohmic heat development would cause a large temperature increase and final destruction of the crystal. The characteristics shown are typical for several successive runs, whereas the first measurement after a long period of time usually shows a shift of the lower threshold voltage to higher values. The general shape of the curves is rather independent of the p_H -value of the solution and of whether the electrolyte solution is stirred or not. However, use of KBr and KI instead of KCl in the electrolyte solution gives significant shifts of the threshold voltage to about 2 V and 1 V respectively.

The photocurrent was measured using chopped light of high intensity. Therefore the dark current could be clearly separated from the photocurrent even at voltages as high as 100 V, where the dark current is comparable to the photocurrent. A saturated primary photocurrent was observed over the whole voltage range with no indication of a

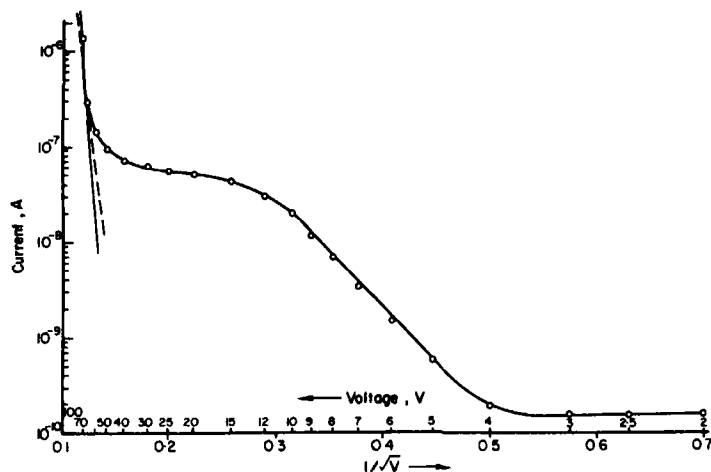


Fig. 2. Typical current-voltage characteristic. The current is plotted on a logarithmic scale against the reciprocal of the square root of the voltage. Electrolyte is a 2 M KCl solution with acetate buffer $p_H = 4.5$.

current increase when the crystal was illuminated with light of a wavelength of 3700 Å or shorter.*

(b) *Properties of the ZnO and the depletion layer*

(1) *Conductivity and Hall-effect.* Hall-effect and conductivity were determined with the van der Pauw method in the temperature range from liquid nitrogen up to room temperature. Performing an analysis of the statistics in terms of a single donor level at an energy E_d below the conduction band, the expression for the carrier concentration is

$$\frac{n^2}{(N_D - n)N_c} = \frac{(m^*)}{m} \cdot \frac{1}{D} \exp(-E_d/kT)$$

where N_D is the donor concentration, D the donor degeneracy, N_c the effective density of states and m^* the effective density of states mass of the conduction band. From the logarithmic plot of n vs. $1/T$ the energy E_d is

*Similar curves to those reported by Williams[5] were observed for white light or light of wavelength between 3750–4000 Å. A detailed report on the investigation of the photocurrent is presented elsewhere[6].

found to be 0.05 eV. This agrees with the value determined by Hutson[7] for zinc (or hydrogen) donors. The concentration of the donors was estimated from the flattening of the $\log n$ vs. $1/T$ curve at room temperature and found to be approximately $2 \cdot 10^{16} \text{ cm}^{-3}$. The room temperature mobility was $180 \text{ cm}^2/\text{Vsec}$ in agreement with values reported in the literature, though below 165°K strong impurity scattering reduced the mobilities below those reported in Hutson's paper.

(2) *Charge measurement.* We have examined the charge resulting from switching on and off the voltage. For this purpose a small resistor ($10^3 \Omega$ or $10^4 \Omega$) was placed in series with the sample. If the discharge current of the capacitance is to flow through the resistor, the value of the resistor must be small compared to the internal resistance of the capacitor. This was checked by varying the values of the resistor. In order to obtain the charge, the transient currents were integrated, the integration times being in the order of seconds. The contribution to the charge from steady state currents could be identified from the linear increase of the charge with time and it was consequently subtracted. The general

features of the charge measurement as a function of voltage are illustrated in Fig. 3. The results presented there should reflect the charging and discharging of the space charge capacitance. The charges at turn on and off are approximately the same below 5 V, whereas above this critical voltage an excess charge at turn on is observed. This excess charge consists above 10 V of a constant, voltage independent charge and a contribution which is proportional to $V^{1/2}$. The charge at turn off above 10 V increases only slightly with voltage. This is a rather astonishing fact because one expects that the crystal is in the same state before and after application of the voltage and therefore the transported charges should be the same.

Initially about one order of magnitude less charge was transported in the voltage range below 20 V with ΔQ_{sc} proportional to $V^{1/2}$. At this voltage a sudden increase in the transported charge occurred. After this forming process the curves shown in Fig. 2 could be reproducibly measured. After a waiting period

of several hours without applied voltage the original curve could be measured again. The origin of this forming process and especially the recovery of the crystal are not understood at the present time.

Following a procedure proposed by Many and Katzir[8] the following relation between the voltage V and the transported charge ΔQ_{sc} may be derived for a Schottky barrier

$$\frac{V}{\Delta Q_{sc}} = \frac{\Delta Q_{sc}}{2e\epsilon\epsilon_0 N_+} = \frac{2}{(2e\epsilon_0 N_+ e)^{1/2}} \cdot V_0^{1/2}. \quad (1)$$

Here N_+ is the concentration of ionized donors, V_0 the barrier height in the absence of an external voltage.

A plot of $V/\Delta Q_{sc}$ vs. ΔQ_{sc} should give a straight line. The concentration of the ionized donors can be determined from the slope of the straight line and V_0 can be calculated from the intersection with the ordinate. Evaluation of the experimental data can be made only for the low voltage range below 8 V. A plot of $V/\Delta Q_{sc}$ vs. ΔQ_{sc} is shown in Fig. 4. The

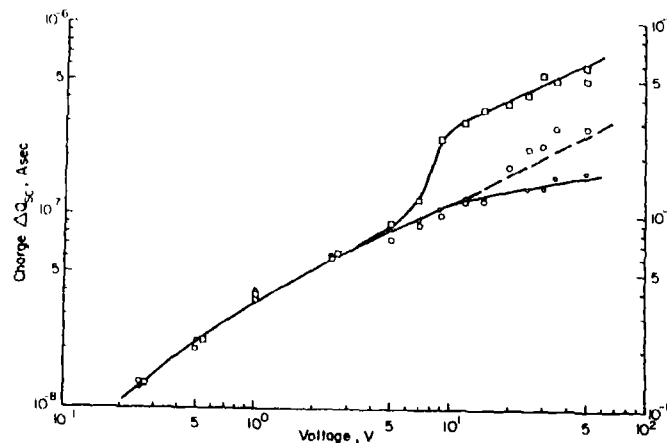


Fig. 3 Charge as a function of applied voltage. The upper and lower curve represents the charge measured upon turn on and turn off resp. The dotted line gives the fast contribution to the transported charge in the turn on mode. This indicates that at the relevant voltages the Schottky barrier is formed before any significant injection of charge carriers takes place. Therefore the emission rate of charge carriers from surface states must be smaller than the thermal emission from the donors in the bulk. Area of the crystal $\sim 0.1 \text{ cm}^2$.

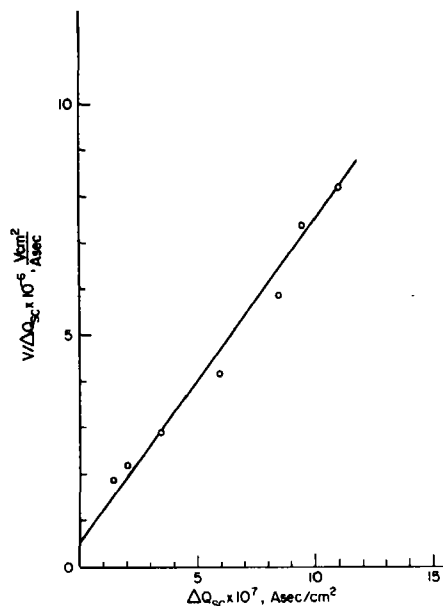


Fig. 4. A plot of $V/\Delta Q_{sc}$ vs. ΔQ_{sc} . Here Fig. 3 is replotted in order to give a more accurate evaluation of the experimental data.

straight line proves that the depletion layer is a true Schottky barrier. The ionized donor concentration was found to be in this case $8 \times 10^{17} \text{ cm}^{-3}$, and the equilibrium barrier height V_0 about 0.008 V. Though the results of the different measurements always indicated that a Schottky barrier is formed at the surface, the value of the donor concentration and of V_0 were found to vary between $0.4\text{--}1 \cdot 10^{18} \text{ cm}^{-3}$ and 0.008–0.05 V respectively. This is probably due to an inhomogeneous donor distribution in the crystal.

The same evaluation of the experimental data in the voltage range below 20 V can be made for the initial measurement. One finds in this case a donor concentration of $2 \cdot 10^{16} \text{ cm}^{-3}$ and for V_0 a value of 0.38 V. The values for V_0 for both the formed and original crystal, were in agreement with the results of the photocurrent measurements.

(3) *Transient current data.* In order to learn more about the depletion layer in the

voltage range in which the charge at turn off is nearly voltage independent, current on turning off the voltage was investigated. The analysis of experimental data is based on the assumption that a Schottky barrier exists. If C is a voltage dependent Schottky capacitance, and R a resistor in parallel, the current in this circuit upon switching off the voltage is given by

$$\frac{dQ}{dt} = \frac{d(CV)}{dt} = \frac{V}{R}. \quad (2)$$

The Schottky capacitance is a function of voltage. One finds

$$C = \frac{Q}{V} = \frac{(2\epsilon\epsilon_0 \cdot \rho)^{1/2}}{V}. \quad (3)$$

Here ρ is the space charge density.

Insertion of this expression into equation (2) and integration gives

$$I = \frac{V_i}{R} \frac{1}{(1 + t/RC_0)^2} \quad (4)$$

where C_0 is the Schottky capacitance at the initial voltage V_i .

A typical example of a discharge curve is shown in Fig. 5. The applied voltage was 40 V. Current and time are both plotted logarithmically. The first rapid decrease of the current is seen as a straight line with a negative slope of two. This is to be expected for a Schottky capacitance. It is valid for currents down to 3 per cent of the initial current. Thereafter a slowly decreasing current is observed. Evidently most of the charge is transported in the latter process because the times involved are orders of magnitude larger than those due to the fast discharging process of the Schottky capacitance. A peak in the current shows up in the millisecond region. It is barely observable in this logarithmic representation, though it is quite clearly resolved if a linear current-time scale is used. It is probably connected with the regeneration of surface states.

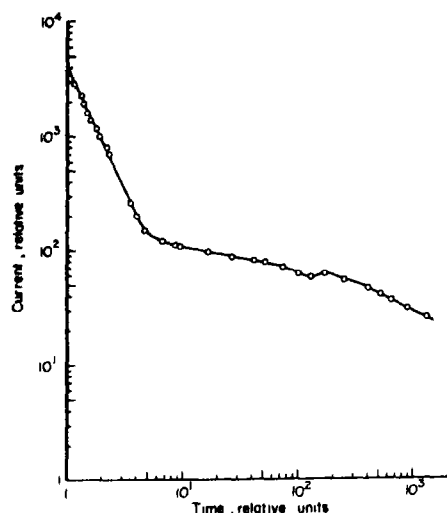


Fig. 5. Discharge curve, current vs time on a logarithmic plot ($1 + t/RC_0$) is plotted on the abscissa. $RC_0 = 3.8 \mu\text{sec}$, $R = 10^4 \Omega$, d.c. bias 40 V and the area of the crystal 0.05 cm^2 .

The fast discharging process was numerically evaluated with the above formula[4]. The value for C_0 was 7.6 nF/cm^2 and from this the donor concentration was calculated to be $1 \cdot 10^{16} \text{ cm}^{-3}$, a value which is much smaller than the one derived from the charge measurements.

(4) *Capacitance data.* In order to substantiate the transient and charge measurements, the differential capacitance was measured for a bias voltage range from 0.5 V–70 V. The result is plotted in Fig. 6, using logarithmic rather than the usual linear scales for both capacitance and voltage. The voltage dependence can thus be clearly determined over the whole voltage range of two orders of magnitude. The capacitance decreases only slightly with voltage below about 4 V. Between 4–8 V an anomalous sharp drop in capacitance occurs. Above 8 V a $V^{-1/2}$ dependence is observed, which is to be expected for a Schottky depletion layer. Numerical evaluation of this high voltage regime, using

$$\text{for } C_{\text{diff}} = \frac{dQ}{dV} = \left(\frac{\epsilon \epsilon_0 e N_+}{2V} \right)^{1/2}, \text{ gives a concentration of ionized donors of } 1.6 \times 10^{16} \text{ cm}^{-3},$$

a value which is in fair agreement with the one determined from the transient measurements and from Hall effect data.

4. DISCUSSION AND CONCLUSIONS

(a) *Physical model of the depletion layer*

The sharp increase in current with voltage could be in principle due to three phenomena: impact ionization, Schottky emission or tunnelling from surface states.

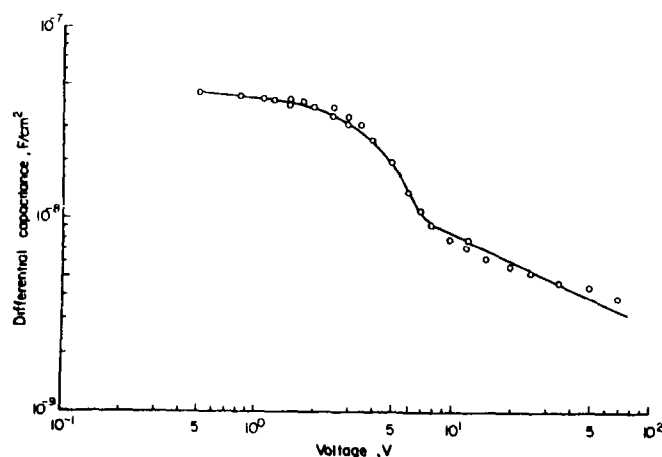


Fig. 6. Differential capacitance as a function of d.c. bias. The frequency of the a.c.-signal was 100 c/s.

Impact ionization in the depletion layer can be ruled out because of the observation of saturated photocurrents. Therefore it is believed that the only explanation for the strong current increase is an injection of charge carriers from surface states. This is substantiated by the charge measurements, the transient current and the differential capacitance data. From the charge measurements we conclude that in the voltage region from 1–8 V a Schottky depletion layer exists with an ionized donor concentration of about $8 \cdot 10^{17} \text{ cm}^{-3}$.

Above 8 V the charge at turn on is obviously composed of two independent contributions: the charge stored in the space charge capacitance and the charge injected from surface states. Significantly this charge injection is observed in a voltage range which coincides with the one in which the current flattens in the case of the d.c.-measurement. From this coincidence it is concluded that the injection of the charge carriers for both phenomena takes place from the same energy level. As a direct current flows, an electrochemical transfer process must occur which opposes the emptying of the surface states and the steady state electron concentration in the depletion layer must be higher than at voltages below 8 V. This increase in electron concentration has an important consequence. At low voltages the concentration of ionized donors is due to the total concentration of deep and shallow donors. This is so because the electron concentration in the depletion layer is practically zero at low voltages and therefore the space charge density will be only determined by the emission of electrons from the deep and shallow donors, the recapture of electrons by these centers being negligible. Hence after a sufficiently long waiting time, inversely proportional to the emission rate, all donors will be ionized.

By injection from surface states the electron concentration in the depletion layer is increased and capture of electrons by deep

donor centers shifts the space charge density to lower values. Hence the field at the surface and the injection current will be lowered. At a sufficiently high injection rate, the shallow donors only will form the space charge in the bulk, and the deep donors will contribute to the space charge density only close to the surface, i.e. the depletion layer will split up into a part with high and a part with low space charge density. Therefore, on turning off the voltage the transported charge should be smaller by the amount of charge which is now stored in deep donor centers. This lack of charge is clearly demonstrated by the experiments.

The arguments put so far can only be applied if the following assumptions are physically meaningful:

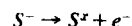
(a) The thermal emission rate ($\alpha_{S \text{ thermal}}$) of electrons from the surface states must be smaller than the thermal emission rate ($\alpha_{B \text{ thermal}}$) from deep donors in the bulk. This gives the condition

$$\alpha_{B \text{ thermal}} > \alpha_{S \text{ thermal}} \text{ at low fields.}$$

(b) At high fields the field emission rate for the surface states must be higher than the thermal emission rate, while the reverse must be true for the donors. Hence

$$\alpha_{B \text{ thermal}} > \alpha_{B \text{ field}} \text{ and } \alpha_{S \text{ field}} > \alpha_{S \text{ thermal}} \text{ at high fields.}$$

These assumptions are not unrealistic for the case under consideration. For the surface states S the emission of an electron may be described by the reaction



and for the donors $D^x \rightarrow D^+ + e^-$.

Therefore electron emission leaves the surface state neutral and the donor state positive. The capture cross section σ_n of a positive centre may be easily 3 orders of magnitude larger than that of a neutral centre [9]. Applying thermodynamic and kinetic considerations [10] one is able to show that the capture cross section and the thermal emission rate are connected by the following equation

$$\alpha_{\text{thermal}} = N_c v_n \sigma_n \cdot e^{-\Delta E/kT}.$$

Here v_n is the thermal velocity of the electron and ΔE the energy separation of the donor or surface state from the conduction band. This formula shows, that even for the same value of ΔE , the thermal emission rate from the donor may be three orders of magnitude larger simply due to the larger capture cross section for electrons. Therefore condition (a) is no severe physical restriction. The difference in thermal emission rate affects also the

observability of a field assisted emission from the center. Clearly an enhanced emission from the surface states will be observed before this is possible for a field enhanced emission from the donors. This condition (a) implies condition (b), even under the assumption of equal fields at the surface and in the bulk.

The drop in space charge density under sufficiently high injection rate is also directly confirmed by the transient current data and the differential capacitance measurements at high voltages. From both measurements an ionized donor concentration of $1-2 \cdot 10^{16} \text{ cm}^{-3}$ was determined, a value much smaller than the one derived from the charge measurements at low voltages. Applying the physical arguments outlined before, we must conclude that the high concentration of $8 \cdot 10^{17} \text{ cm}^{-3}$ is mainly due to deep donors, whereas the concentration of $1-2 \cdot 10^{16} \text{ cm}^{-3}$ is due to shallow donors. These shallow centers, observed also in the Hall effect measurements, are most likely due to ionized Zn.

At low voltages the differential capacitance does not show the $V^{1/2}$ dependence of a Schottky barrier. Therefore the concentration of the donors at low voltages cannot be determined from these measurements, though the anomalous drop in capacitance between 4-8 V indicates qualitatively the decrease in space charge density. The behaviour of the differential capacitance at low voltages is determined by the fact that both deep and shallow centers form the depletion layer and so no equilibrium is established between the electrons and the ionized deep donors in a time comparable to the period of the a.c.-signal used for the capacitance measurements. This will be discussed in more detail in the Appendix.

(b) Discussion of the I - V characteristic

If Schottky emission were the dominant injection process and the cause for the sharp increase in current with voltage, then the current-voltage characteristic should, according to theory [11], be linear in a plot of $\log j$ vs. $V^{1/2}$. This is not in fact observed. If the

injection is due to tunnelling, we have according to the theoretical treatment of Franz [12]

$$j = evN_s \exp \left(-\frac{4\sqrt{2m^*E_s}^{3/2}}{3hF_s} \right) \quad (5)$$

where N_s is the density of surface states, ν a frequency factor, e the electronic charge, m^* the effective mass, E_s the energy of the state below the conduction band, h Planck's constant, and F_s the electric field strength, in our case the field right at the surface. The justification for the use of the highest field in the depletion layer lies in the fact that the field at the surface is practically constant within a tunnelling distance. The expression (5) is only valid if the surface state is neutral after emission of the charge carrier. Otherwise correction terms for the image force must be taken into account, which would increase the tunnelling probability.

In a Schottky barrier F_s is proportional to the square root of the applied voltage. Making use of this we see that a plot of $\log j$ vs. $V^{-1/2}$ should yield a straight line. This is actually true in the voltage range from 4 to 10 V as can be seen in Fig. 2. The electric field at the surface can be calculated from Gauss' law.

$$F_s = \frac{Q_{sc}}{\epsilon\epsilon_0} = \left(\frac{2eN_+V_s}{\epsilon\epsilon_0} \right)^{1/2} \quad (6)$$

where Q_{sc} is the total space charge per unit area, the value of which was obtained from

$$Q_{sc} = (2e\epsilon\epsilon_0N_+)^{1/2}V_s^{1/2}. \quad (7)$$

The concentration of ionized donors is about $8 \cdot 10^{17} \text{ cm}^{-3}$ for a bias less than 10 V. With this value for N_+ the experimental data can be fitted to equation (5) and the energy E_s of the surface state was found to be 0.58 eV. The same result was obtained whether the electrolyte solution contained KCl, KBr or KI. This indicates that in all cases the tunnelling takes place from the same surface state.

The flattening of the curve above 20 V may

have two causes. Firstly, injection of charge carriers reduces the space charge density in the depletion layer due to the capture of electrons by deep centers. Therefore F_s does not increase with voltage as strongly as expected (equation (6)), and hence the same must be true for the tunnelling current. Secondly the regeneration rate of the surface states might be the rate limiting process, thereby restricting the current to a certain value. In the latter case the current increase, which is observed above 30 V, should be due to a second, deeper surface state.

A clear cut experimental distinction between the two mechanisms is not possible, because the current fluctuated strongly at voltages above 70 V. Despite this uncertainty the experimental curve is tentatively approximated by a straight line above 40 V. If one uses the fact that in this high voltage range a Schottky barrier also exists, however, with a concentration of ionized donors of $2 \cdot 10^{16} \text{ cm}^{-3}$, the experimental data can again be used to calculate the energy of the surface state, from which the tunnelling is to occur. The value for E_s is 0.56. It is close to the value determined from the current increase in the low voltage range. Therefore it is very likely that the tunnelling occurs from the same surface state and that the flattening of the curve is mainly due to a reduction in the surface field.

The nature of the surface states involved in the observed tunnelling process is not clear. As the experimental results are practically independent of the composition of the electrolyte, it is felt that no direct transfer of electrons occurs from donors in the solution to the conduction band, but rather a two step process involving tunnelling of charge carriers from surface states (e.g. chemisorbed oxygen) to the conduction band and a subsequent chemical reaction at the surface of ZnO.

Acknowledgements—The author would like to thank W. J. Merz for his continuing interest in this work and F. Stöckmann for stimulating discussions and critical remarks. Helpful suggestions of D. Hauenstein are also gratefully acknowledged.

REFERENCES

1. DEWALD J. F., *Bell Syst. tech. J.* **39**, 615 (1960).
2. GERISCHER H., *J. electrochem. Soc.* **113**, 1174 (1966).
3. MORRISON S. R. and FREUND T., *J. chem. Phys.* **47**, 1543 (1967).
4. HAUFFE K. and RANGE J., *Z. Naturf.* **23b**, 736 (1968).
5. WILLIAMS R. and WILLIS A., *J. appl. Phys.* **39**, 3731 (1968).
6. KIESS H., *J. Phys. Chem. Solids* **31**, 2391 (1970).
7. HUTSON A. R., *J. Phys. Chem. Solids* **8**, 467 (1959).
8. MANY A., *J. Phys. Chem. Solids* **26**, 587 (1965).
9. ROSE A., *Concepts in Photocond. and Allied Problems*, p. 118. Interscience, New York (1963).
10. SCHOTTKY W., *Halbleiterprobleme I*, p. 138. (1954).
11. STÖCKMANN F., *Phys. Status Solidi* **3**, 221 (1963).
12. FRANZ W., *Handbuch der Physik*, Vol. 17, p. 155 (1956).

APPENDIX

It is shown here, that in the presence of shallow and deep donors the voltage dependence of the differential capacitance deviates from the ideal Schottky behaviour. This is to be expected if the shallow donors respond to the a.c.-signal, whereas the deep donors do not.

We have to distinguish several voltage regimes:

(a) *Low voltages*. It is assumed here, that only shallow donors form the space charge, whereas the deep donors are still below the Fermi level (compare Fig. 7(a)). This assumption applies for voltages $V_0 < V < \frac{E_F - E_d}{e} - V_0$

where V_0 is the barrier height in the absence of an applied voltage, and $(E_F - E_d)$ is the energy separation of the deep donors from the Fermi level.

(b) *High voltages*. The deep donors are now assumed to be above the Fermi level in a part of the depletion layer (see Fig. 7(b)). Therefore the depletion layer consists of two parts, in one of which the space charge density is given by the density of ionized deep and shallow donors, whereas in the other part the shallow donors only contribute to the space charge density. The boundary between the two parts is at a potential of approximately $\varphi_b = \frac{E_F - E_d}{e} - V_0$. Hence the applied voltage is supposed

to be $V > \frac{E_F - E_d}{e} - V_0$.

After application of the voltage the equilibrium between capture and emission of electrons from the donors is disturbed because the surface layer is depleted. The centres will become ionized after a time which is determined by the thermal emission rate. For shallow donors this time is short, for deep donors however, it may be easily of the order of seconds. A small a.c. signal, with a frequency even as low as 100 c/s, therefore changes only the occupancy of the shallow centres. Thus it seems to be appropriate in this voltage regime to calculate the voltage dependence of the differential capacitance under the assumption that both deep and shallow centres form the depletion layer due to a d.c. bias, but that only the shallow

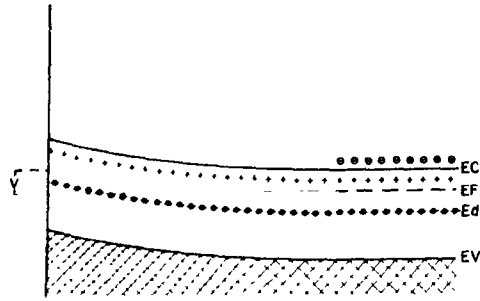


Fig. (a)

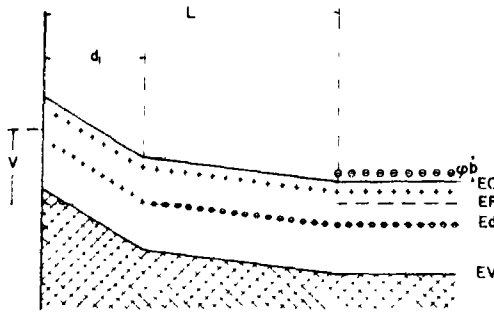


Fig. (b)

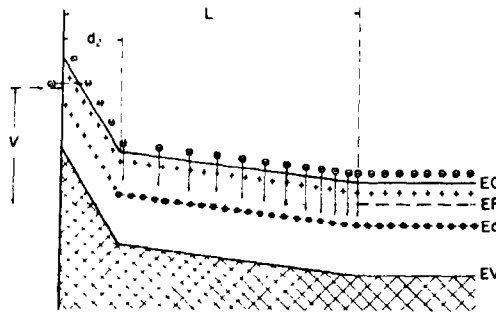


Fig. (c)

Fig. 7. (a) Schematic band diagram at low voltages. Only shallow donors contribute to the space charge. (b) Band diagram at high voltages without injection. Close to the surface deep and shallow donors contribute to the space charge. At distances $x > d_1$ the space charge is formed by shallow donors. d_1 increases with increasing voltage. (c) Band diagram at high voltages with injection. Deep and shallow donors form the space charge close to the surface, whereas for $x > d_2$ shallow donors only are ionized. d_2 decreases with increasing voltage because d_1 is determined by the injection level. If no injection would occur at the relevant voltage the depletion layer width L would be smaller than shown in the diagram for the case with injection.

donors respond to the a.c. signal which is used for measuring the differential capacitance.

(c) *High voltages with injection of charge carriers into the depletion layer.* In this case the density of free charge carriers is increased in the depletion layer. Capture of electrons by deep donor centres shifts the space charge density to lower values. This will predominantly occur at distances $x > d_2$ from the ZnO-electrolyte interface; beyond d_2 the electron density is above a certain level and influences therefore the occupancy of the deep donor centres (Fig. 7(c)).

Let us now consider the different voltage regimes:

(a) The capacitance in the low voltage regime is clearly identical with the Schottky capacitance and it does not need any further comments.

(b) In this voltage regime the depletion layer divides into two parts and we have Poisson's equation:

$$\frac{dF}{dx} = \frac{e}{\epsilon\epsilon_0} (N_d + N_s) \text{ for } 0 \leq x \leq d_1 \quad (8)$$

$$\frac{dF}{dx} = \frac{e}{\epsilon\epsilon_0} N_s \text{ for } d_1 < x \leq L. \quad (9)$$

Here F is the field strength, N_d and N_s the concentration of deep and shallow donors resp., L the width of the depletion layer and d_1 the point at which the potential has the value ϕ_b . The boundary conditions are:

$$\begin{aligned} x = L; F = 0 \text{ and } x = 0; \phi = -V \\ x = L; \phi = 0. \end{aligned}$$

After an elementary calculation one finds the following relationships:

$$F_s = \frac{eN_d d_1}{\epsilon\epsilon_0} + \frac{eN_s L}{\epsilon\epsilon_0} \quad (10)$$

F_s is the field strength at the surface

$$V = \frac{eN_d}{\epsilon\epsilon_0} \cdot \frac{d_1^2}{2} + \frac{eN_s L^2}{\epsilon\epsilon_0} \quad (11)$$

$$Q_{sc} = eN_d d_1 + eN_s L \quad (12)$$

$$L = \frac{\epsilon\epsilon_0}{e(N_d + N_s)} \cdot F_s + L_0 \quad (13)$$

with

$$L_0 = \frac{N_d}{N_d + N_s} \left(\frac{2\phi_b \epsilon\epsilon_0}{eN_s} \right)^{1/2}$$

$$\begin{aligned} L = \frac{N_d}{N_d + N_s} \cdot \left(\frac{2\epsilon\epsilon_0 \phi_b}{eN_s} \right)^{1/2} + \frac{1}{2} \left[\left(\frac{N_d}{N_d + N_s} \right)^2 \cdot \frac{8\epsilon\epsilon_0 \phi_b}{eN_s} \right. \\ \left. + \frac{8\epsilon\epsilon_0 V}{e(N_s + N_d)} - \frac{8\epsilon\epsilon_0 \phi_b N_d}{eN_s(N_d + N_s)} \right]. \end{aligned} \quad (14)$$

As the deep donors do not respond to the a.c. signal one finds

$$C = \frac{dQ_{sc}}{dV} = eN_s \cdot \frac{dL}{dV} = \frac{\epsilon\epsilon_0}{L(V)}. \quad (15)$$

Equation (14) gives with $N_d \gg N_s$

$$C = \frac{(\epsilon\epsilon_0 e N_d)^{1/2}}{V^{1/2} \left(1 + \left[\frac{N_d}{N_s} \cdot \frac{\varphi_b}{V}\right]^{1/2}\right)}$$

Hence

$$C = \left(\frac{\epsilon\epsilon_0 e N_s}{2\varphi_b}\right)^{1/2} = \text{const. if } \varphi_b < V < \frac{N_d}{N_s} \cdot \varphi_b \quad (16)$$

and

$$C = \left(\frac{\epsilon\epsilon_0 e N_d}{2V}\right)^{1/2} \sim \frac{1}{V^{1/2}} \text{ if } \frac{N_d}{N_s} \varphi_b < V. \quad (17)$$

(c) If injection is assumed to occur at high voltages then the depletion layer divides also in a part with high and low space charge density. Equations (8) and (9) including the boundary conditions are valid, however d_1 has to be replaced by d_2 which represents now the distance from the surface at which the electron density has the value n_{cr} . For larger distances is $n > n_{cr}$ and therefore the trapping of charge carriers is significant. It is assumed that for $x > d_2$ only shallow donors form the space charge. Using the continuity equation we find a critical field strength

$$F_{cr} = \frac{j}{e\mu_n n_{cr}}$$

Using for j the tunnelling current (equations (5) and (6)), gives

$$F_{cr} = \frac{\nu N e^{-(\alpha/F_s)}}{\mu_n n_{cr}} \text{ with } \alpha = \frac{4\sqrt{2m^*} E_s^{3/2}}{3h}.$$

Integration of equation (8) gives

$$F_{cr} = F_s - \frac{e}{\epsilon\epsilon_0} (N_d + N_s) d_2$$

and hence

$$d_2 = \frac{\epsilon\epsilon_0}{e(N_d + N_s)} \left(F_s - \frac{\nu N}{\mu_n n_{cr}} e^{-(\alpha/F_s)} \right). \quad (18)$$

Replacing d_1 by d_2 in equation (10) we find L as a function of F_s

$$L = \frac{\epsilon\epsilon_0 F_s}{e N_s} - \frac{\epsilon\epsilon_0 \cdot N_d}{e N_s (N_d + N_s)} \left(F_s - \frac{\nu N}{\mu_n n_{cr}} e^{-(\alpha/F_s)} \right). \quad (19)$$

At low fields the exponential term in equation (19) may be neglected.

Then

$$L = \frac{\epsilon\epsilon_0}{e} \cdot \frac{F_s}{N_d} \text{ and hence } L = \left(\frac{2\epsilon\epsilon_0 V}{e N_d} \right)^{1/2}.$$

At high fields, when the injection current becomes sufficiently high, d_2 becomes very small and from equation (19) we find

$$L = \frac{\epsilon\epsilon_0 F_s}{e N_s} \text{ and therefore } L = \left(\frac{2\epsilon\epsilon_0 V}{e N_s} \right)^{1/2}. \quad (20)$$

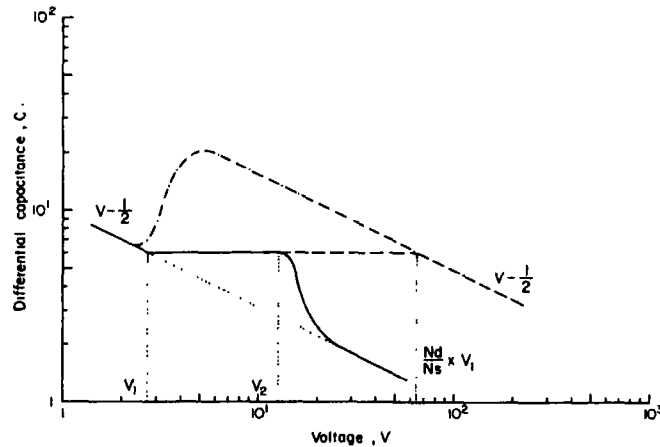


Fig. 8. Differential capacitance as a function of d.c.-bias for the two centre model as discussed in the Appendix. Up to V_1 the low voltage regime is valid, the voltage regime $V_1 \leq V \leq V_2$ represents the high voltage regime without injection of charge carriers. If no injection would occur for $V > V_2$ the dashed line would represent the voltage dependence of the capacitance. Under injection of charge carriers the capacitance drops to a value which is determined by the shallow donors. This is shown by the solid line for voltages $V > V_2$. The dashed and dotted line gives the capacitance as a function of voltage if shallow and deep donors respond to the a.c. signal as calculated by Dewald [1].

Making use of equation (15) one finds that at high fields, when the injection is significant

$$C' = \left(\frac{\epsilon\epsilon_0 e N_d}{2V} \right)^{1/2}$$

The voltage dependence derived from this model is schematically shown in Fig. 8, having in mind that equation (19) is only valid if $(L - d_2) > L_0$ i.e. that the density of the injected electrons at $(L - L_0)$ is comparable to the equilibrium density of electrons at this point.

HIGH FIELD BEHAVIOUR OF ZnO-II INVESTIGATION OF THE PHOTOCURRENTS

H. KIESS

Laboratories RCA, Ltd., Zurich, Switzerland

(Received 29 December 1969)

Abstract—Photocurrents in ZnO have been investigated under high field conditions. An anomalous increase of photocurrent with voltage was observed at wavelengths between $\lambda = 3750 \text{ \AA}$ and $\lambda = 3900 \text{ \AA}$. It is shown that this increase in photocurrent is due to a photoinduced increase in the tunnelling rate of charge carriers from surface states.

IN THE past photocurrents in the system ZnO-electrolyte[1-4], have been investigated by many people mostly with the aim of obtaining information about chemical transfer reactions. Williams and Willis[5] were the first to report about the transport mechanism of photoexcited charge carriers in ZnO using an electrolyte as blocking contact and as a means of achieving high electric fields in the ZnO surface layer adjacent to the electrolyte. They found a strong increase in photocurrent at high voltages and concluded that impact ionization across the band gap causes the photocurrent to rise steeply. It is the intention to show here that an anomalous increase in photocurrent is not necessarily due to impact ionization and that some care must be taken in the interpretation of experimental results. For the ZnO single crystals used in the work presented here, it is shown that another mechanism is responsible for the strong increase in photocurrent. The ZnO single crystals were obtained from the 3M company and came from the same batches as used in a former investigation[6] on the high field behaviour of ZnO. The crystals were prepared as in the above work. For the experiments the crystals were mounted in a way which exposed one face to the electrolyte which formed the blocking contact with the ZnO. The other face was provided with an ohmic In-contact. The crystals were illu-

minated through the electrolyte for photocurrent measurements. A Sylvania iodine quartz lamp (700 W) or an Osram high pressure mercury lamp HBO 200 was used with a conventional monochromator or band pass filters for varying the wavelength of the incident light. The illumination of the crystal at different wavelengths was usually reduced to equal incident photon flux by varying the lamp voltage. The calibration was made with an Eppley thermo-pile and a Keithley 148 nanovoltmeter. The photocurrents were recorded with a Moseley 135 x-y recorder. In most cases an acetate buffered 2 M KCl solution with $p_H \sim 4.5$ was used as electrolyte. Variation of the electrolyte solutions and of the p_H -value did not have a significant influence on the results.

Figure 1 shows the photocurrent as a function of the positively biased crystal. The applied voltage is recorded on the horizontal axis and the current on the vertical axis. This recorder trace was obtained using chopped light, which allows the separation of the photocurrent from the dark current provided that the chopping period is longer than the decay or rise time of the photocurrent. Using white light the photocurrent is nearly constant up to 130 V and rises sharply at higher voltages. Significantly the sharp rise of the photocurrent is connected with a strong increase in 'dark current'. Using monochromatic light of wave-

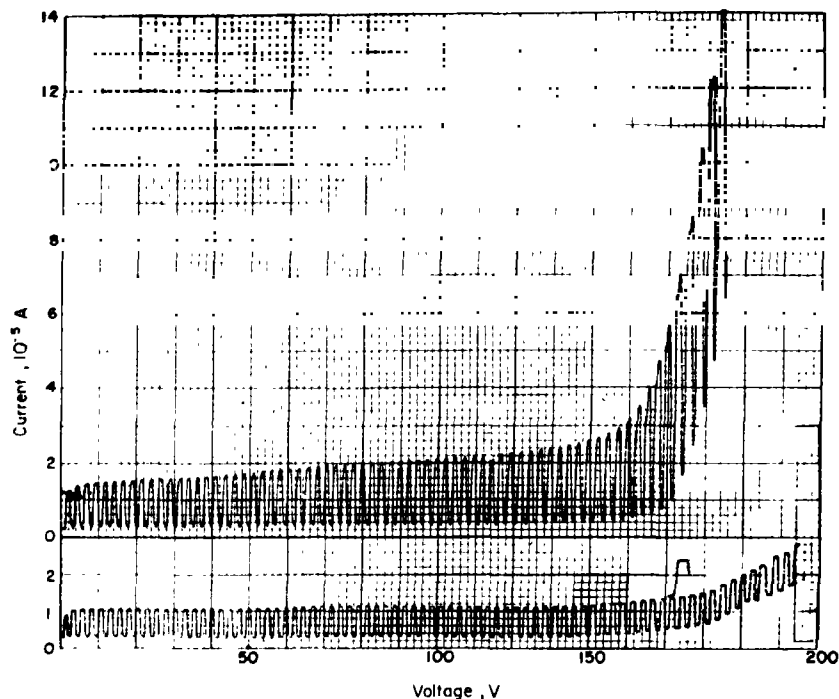


Fig. 1. Photocurrent excited by chopped light as a function of reverse bias. The lower recorder trace was gained with light of wavelength $\lambda = 3650 \text{ \AA}$, the upper recorder trace with white light. The scales for the current and the voltage are identical for both recorder traces. The photocurrent at $\lambda = 3650 \text{ \AA}$ shows a pronounced saturation; the dark current increases from 10^{-6} A at 150 V to $1.7 \cdot 10^{-5} \text{ A}$ at 200 V. With white light a strong increase in photocurrent with voltage is observed. At 150 V the dark current is also about 10^{-6} A , but at 180 V an apparent 'dark current' of $8 \times 10^{-5} \text{ A}$ is observed, which is about one order of magnitude higher than the dark current measured in the low recorder trace.

length $\lambda = 3650 \text{ \AA}$, there are two striking differences: firstly, no increase in photocurrent is observed and secondly, the dark current remains below the value of the apparent 'dark current' which is found in the off periods under illumination with white light. The spectral dependence of the photocurrent-voltage characteristic is shown in Fig. 2, both plotted logarithmically. The photocurrents at different wavelengths were measured with equal incident photon flux, the light intensities being about two orders of magnitude smaller than those of Fig. 1. The photocurrents represent the steady state values. For short wavelengths ($\lambda < 3700 \text{ \AA}$) the photocurrent is independent of voltage apart from

the small increase at voltages below about 2 V). At longer wavelengths it increases with voltage and especially at $\lambda = 3800 \text{ \AA}$ and $3850 \text{ \AA}$ exceeds the saturated photocurrent at shorter wavelengths. As the quantum efficiency defined as transported charge carriers per absorbed photon, was found to be unity at short wavelengths ($\lambda < 3750 \text{ \AA}$), it must be greater than one at the long wavelengths between $3750\text{--}3900 \text{ \AA}$. When the photocurrents were measured in the same way as in Fig. 1, using chopped light, then an apparent 'dark current' was also observed at wavelengths greater than $3750 \text{ \AA}$. The threshold voltage for the increase in both photocurrent and apparent 'dark current'

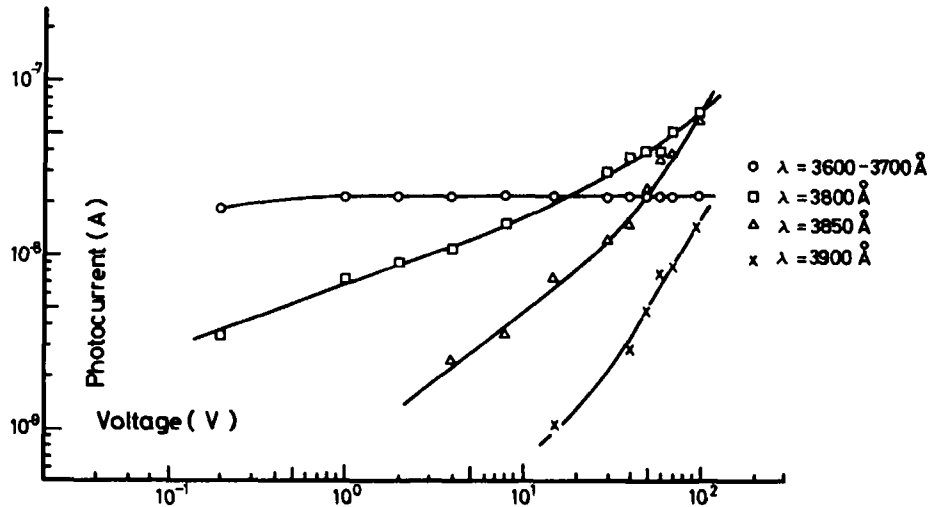


Fig. 2. Photocurrent as a function of reverse bias at different wavelengths. The incident light intensities are reduced to equal photon flux.

is shifted to lower voltage for lower light intensities.

At high voltages the rise and decay time of the photocurrent on switching on and off the light is different for short and long wavelengths. At low voltages rise and decay times of the photocurrent for all wavelengths are below the response time of the recorder. At high voltages and at wavelengths greater than $3750 \text{ \AA}$, however, the photocurrent rises rapidly only to a certain value and then increases with a time constant of about 1–10 sec to higher values. In Fig. 3 the fast component and the steady state value of the photocurrent are plotted as a function of voltage. The fast component of the photocurrent saturates at a value which corresponds to a quantum efficiency of one, whereas the slow component represents an additional current which is not observed under illumination at $\lambda < 3750 \text{ \AA}$.

It is obvious that the results of our measurements exclude the possibility of impact ionization, because no current increase beyond a quantum efficiency of one is observed at sufficiently short wavelengths. The increase

with voltage of the fast component of the photocurrent at longer wavelengths as shown in Fig. 3 must be due to the diffusion of electron hole pairs into the depletion layer, to an increase in depletion layer width and to a shift of the absorption edge by the Franz-Keldysh-effect. We will not be concerned with these physical phenomena in this article but restrict our interest to the increase in quantum efficiency due to the slow process.

It is known from studies[6] of the dark I-V-characteristics and from the dependence of the capacitance as a function of positive d.c.-bias, that the sharp rise in dark current is due to tunnelling of charge carriers from surface states. Furthermore it has been established that at low voltages a Schottky barrier exists with a spatially homogeneous concentration of deep and shallow ionized donors of about $8 \times 10^{17} \text{ cm}^{-3}$. At high voltages ($> 10 \text{ V}$), however, the depletion layer consists of a layer with deep and shallow ionized donors right at the surface, adjacent to a layer with shallow ionized donors with a concentration of about $2 \times 10^{16} \text{ cm}^{-3}$. The region with the low concentration of ionized donors is

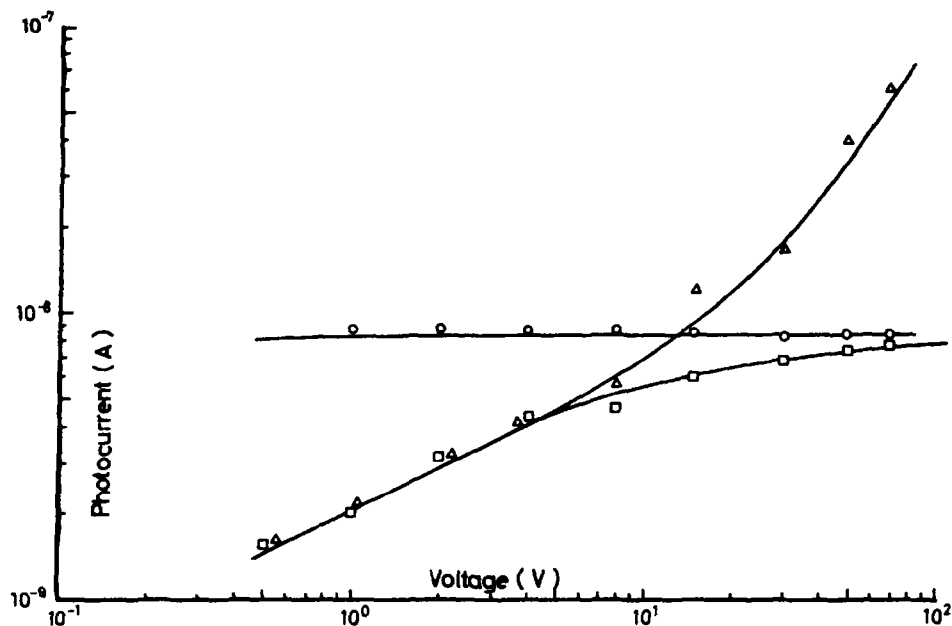


Fig. 3. Photocurrent as a function of voltage at $\lambda = 3800 \text{ \AA}$. The (Δ) refer to the steady state value of the photocurrent and the ($\square$) to its fast component. The horizontal line represents the saturated photocurrent at $\lambda = 3700 \text{ \AA}$.

formed by capture of tunnel-injected electrons by the deep donor centres, leaving only the shallow centres ionized.

Assume now that high voltage ($> 10 \text{ V}$) is applied and that the crystal is illuminated with light of such a wavelength that it penetrates the layer with low ionized donor concentration. Then the following situation arises. Trapping of holes in the region with low donor concentration increases the space charge density there and hence increases the field at the surface. This gives rise to a higher tunnelling rate of charge carriers from the surface states. Therefore a light induced tunnelling current flows through the depletion layer in addition to the recombination free, saturated photocurrent. The magnitude of this tunnelling current depends only on the degree to which the space charge density is increased by the capture of holes. In these circumstances the observed quantum efficiency will be greater than unity. If the penetration depth of the

light is smaller than or equal to the width of the region with high space charge density, the trapping of holes may have an insignificant effect on the space charge density or no trapping at all may be possible, if for example the trapping centres were identical with the deep donors in our ZnO crystals. This mechanism explains the main features of the spectral dependence of the photocurrent and the increase of quantum efficiency above one. It also explains why the increase of photocurrent at low light levels starts at lower voltages, since then the saturated photocurrent is so small that it becomes comparable with the tunnelling current. The question arises whether the trapping of holes can be detected. Supposing the voltage is kept constant and the space charge density is increased by hole trapping, then the total charge stored in the depletion layer also increases. Therefore the charges measured in the dark and under illumination should be different. This was

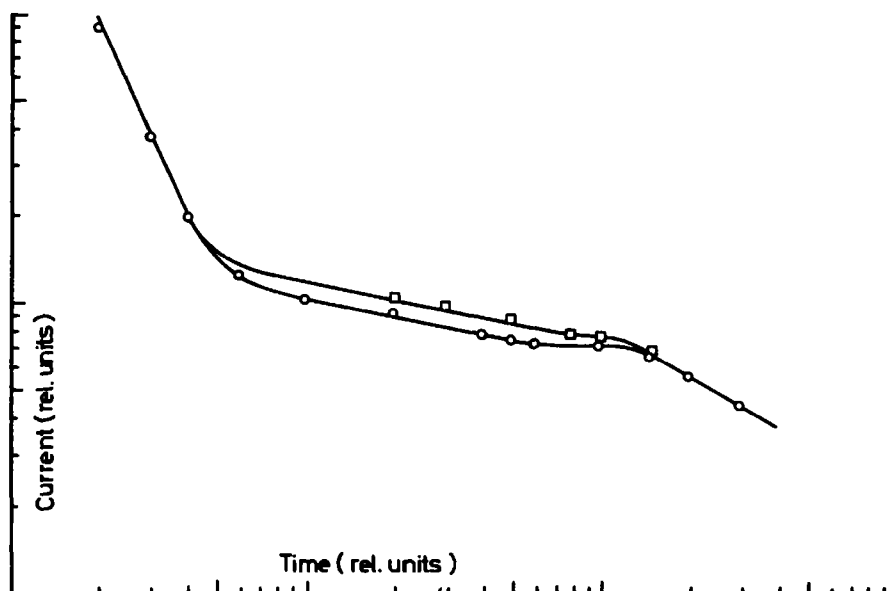


Fig. 4. Transient current on switching off the voltage. The lower curve is observed when the crystal is in the dark or illuminated with light of a wavelength shorter than 3750 Å. The upper curve represents the transient current at $\lambda = 3800$ Å.

actually found. The result is shown in Fig. 4, where the transient current on switching off the voltage is shown. The curve in the dark and under illumination with short wavelength light ($\lambda \leq 3700$ Å) are identical. However, a higher discharge current is observed under illumination with light of wavelength between 3750–4000 Å. The plateau, which shows up in the millisecond region, is not understood up to now, but it is probably connected with the regeneration of the surface states.

Acknowledgements—I would like to thank W. J. Merz and J. Sandercock for suggestions to improve this manuscript.

REFERENCES

1. GERISCHER H., *J. electrochem. Soc.* **113**, 1174 (1966).
2. MORRISON S. R. and FREUND T., *J. chem. Phys.* **47**, 1543 (1967).
3. GOMES W. P., FREUND T. and MORRISON S. R., *J. electrochem. Soc.* **115**, 818 (1968).
4. HAUFFE K., *Rev. pure appl. Chem.* **18**, 79 (1968).
5. WILLIAMS R. and WILLIS A., *J. appl. Phys.* **39**, 3731 (1968).
6. KIESS H., *J. Phys. Chem. Solids* **31**, 2379 (1970).

ULTRASONIC PARAMETERS IN THE BORN MODEL OF THE RUBIDIUM HALIDES

R. W. ROBERTS and CHARLES S. SMITH

Physics Department, University of North Carolina at Chapel Hill, N. C. 27514, U.S.A.

(Received 9 February 1970)

Abstract—Values of all dC/dP have been obtained at 295°K and are strikingly smooth when plotted against nearest neighbour distance, d_0 . When combined with known temperature coefficients of the elastic constants, they lead to values of $\xi = d \ln B_T / dT$, which are uniformly $-1 \times 10^{-4} \text{ deg}^{-1}$ for these crystals with low Debye temperature. The resulting Born model exponential parameters, d_0/ρ , are precisely linear with d_0 , in contrast with d_0/ρ values where compression ξ were used in the necessary correction for vibrational effects. Values of dB_T/dP are uniformly 5.6, a general magnitude well accounted for by the Born model which, however, predicts a significant systematic variation in the four halides. In all these features the Rb halides are similar to the Na and K halides.

1. INTRODUCTION

A PAPER of this title by Roberts and Smith[1] on the sodium and potassium halides appears in a recent issue of this journal. This note reports the experimental measurement of the pressure derivative of the single crystal elastic constants of the rubidium halide sequence. It extends to the rubidium sequence the analysis of the previous paper for the parameters in the Born model in the Hildebrand approximation, and compares these ultrasonically based parameters with previously accepted values derived from compression work. The note also extends to the rubidium halides the discussion of the pressure derivative of the isothermal bulk modulus.

The experimental techniques used, data reduction, analysis, notation and conclusions are largely those of the previous paper; exceptions are noted in appropriate places. The note is also sectioned in a parallel fashion.

2. EXPERIMENT

The experiment results were obtained on [110] single crystals procured from Semi-Elements. The crystals that were used passed our stringent X-ray tests and the sterling cooperation of Mr. Joseph Barrett, formerly of that company, is gratefully acknowledged.

Rubidium fluoride proved to be especially difficult because it is extremely hygroscopic, by far the worst so of the group. This material was handled exclusively in a glove box, but even so, acoustic seals were difficult to make and to retain throughout a pressure run. For this reason, the important pressure effect on the longitudinal wave was verified on a [100] crystal obtained especially for this purpose.

3. RESULTS

Table 1 shows the experimental dC/dP for the longitudinal [110] stiffness, C'_{11} , and the two shear stiffnesses C and C' . Also shown is the result for the adiabatic bulk modulus, B_s , obtained directly by combining the measurements, and for the isothermal bulk modulus, B_T , which was derived from dB_s/dP as described below.

Each row in Table 1 plots smoothly, almost

Table 1. Values of dC/dP at 295°K for the rubidium halides

	RbF	RbCl	RbBr	RbI
C'	6.51	6.88	6.91	7.02
C'_{11}	4.93	5.88	6.03	6.26
C_{14}	-0.70	-0.56	-0.55	-0.51
B_s	5.57	5.48	5.45	5.44
B_T	5.69	5.62	5.59	5.60

linearly, against nearest neighbour distance, d_0 , just as was observed previously for the sodium and potassium halides. It should be noticed further that dB_s/dP and dB_T/dP are each essentially invariant in the sequence.

4. DERIVED QUANTITIES

Table 2 gives the auxiliary thermodynamic data adopted for use in this section and the next. Sources were as in [1] with two exceptions.

Table 2. Basic data at 295°K for the rubidium halides

	d_0 (10 ⁻⁸ cm)	Ω_0 (10 ⁻²⁴ cm ³ molecule ⁻¹)	B_s (kbar)	C_p (10 ⁻¹⁶ erg deg ⁻¹ molecule ⁻¹)	β (10 ⁻⁴ deg ⁻¹)	γ	$T\beta\gamma$ (10 ⁻²)	B_T (kbar)
RbF	2.826	45.13	277	8.421	(0.94)	1.40	3.87	267
RbCl	3.291	71.29	162	8.567	1.03	1.39	4.23	156
RbBr	3.445	81.77	138	8.595	1.08	1.42	4.53	132
RbI	3.671	98.94	111	8.630	1.23	1.56	5.67	105

The important nearest-neighbor distance, d_0 , for RbF was measured on a specimen of our crystal by the National Bureau of Standards X-ray diffraction group under the direction of Mr. Howard E. Swanson; the value shown will appear in a forthcoming section of NBS Monograph 25. This d_0 is 0.4 per cent larger than the old measurement used on Born model analysis [2] and, because it enters the analysis to the fourth power, the change is significant. It has in fact smoothed our Born model parameters and we are most grateful for the willing, and speedy, cooperation of NBS.

The volume thermal expansion coefficients, β , given for RbCl, RbBr, and RbI are the -40°C measurements of Henglein [3], increased by a common 0.04 deg^{-1} to bring them to 295°K . The temperature adjustment was determined by a comparison of the available data for these and other alkali halides as a function of Debye temperature. The common value of the adjustment reflects the low Debye temperature of these materials. The β value for RbF was arrived at by

judicious extrapolation of the β 's of the other three.

Other thermodynamic input data are the $\text{dln}C/\text{dT}_P$ of Haussühl [4] which have been combined to give the $\text{dln}B_s/\text{dT}_P$ shown in Fig. 1. Our dB_s/dP , together with Table 1, then give $\text{dln}B_s/\text{dT}_V$ in the manner the figure shows.

From $\text{dln}B_s/\text{dT}_V$ we obtain $\xi \approx \text{dln}B_T/\text{dT}_V$ by using equation (4) of [1]. The derived ultrasonic ξ shown in Fig. 2 are remarkably

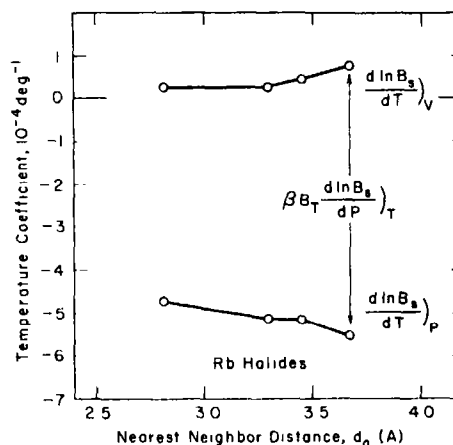


Fig. 1. The temperature coefficients of the adiabatic bulk modulus at 295°K vs. nearest neighbor distance, d_0 .

invariant at $-1 \times 10^{-1} \text{ deg}^{-1}$, again in contrast with values based on temperature and pressure derivatives obtained in compression experiments [2]. The ultrasonic ξ for the Rb sequence are smoother than even those for the Na and K sequences. The Rb halides are essentially classical solids at 295°K ; ξ is

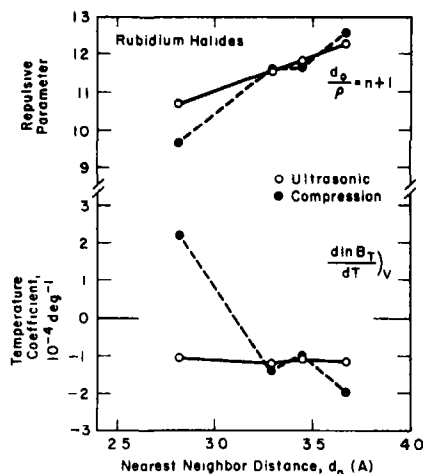


Fig. 2. Derived ultrasonic $\xi = d \ln B_T / dT_V$ at 295°K, and derived Born model repulsive parameter $d_0/\rho = n+1$ vs. nearest neighbor distance, d_0 . Previously accepted values based on compression data are also shown.

uniformly small under these circumstances as Swenson[5] has pointed out for other cubic solids, but it is clearly not zero here.

The second derived quantity, dB_T/dP , was obtained using equation (5) of [1]. The correction involved in going from the adiabatic to the isothermal modulus was again larger than the first approximation suggested by Swenson[5].

5. BORN MODEL

The repulsive interaction that appears in the Born model may be written in a power law version

$$W_R = A \left(\frac{V_0}{V} \right)^{n/3}, \quad (1)$$

or in an exponential version

$$W_R = D \exp \left\{ -\frac{d_0}{\rho} \left[\left(\frac{V}{V_0} \right)^{1/3} - 1 \right] \right\}. \quad (2)$$

Use of the Hildebrand vibrational approximation, the equilibrium condition and the definition of the bulk modulus yields the result,

$$\frac{d_0}{\rho} = n+1 = \frac{4+3\lambda\{1-\xi T\}}{[1-T\beta\lambda]} - 2, \quad (3)$$

together with corresponding expressions for An and $D(d_0/\rho)$, [1]. The quantity λ is $3\Omega_0 B_T / (ae^2/d_0)$ and the curly and square brackets are the vibrational correction terms arising in the Hildebrand approximation which is surely appropriate for the classical Rb halides.

It may be pointed out that either d_0/ρ or $n+1$ is physically the ratio $-r^2 W_R'' / r W_R'$, where r is any crystal distance and the primes signify differentiation with respect to that distance. Values of this quantity are given in Fig. 2. The 'ultrasonic' values employ the ultrasonic ξ , of the lower part of the figure, in the curly bracket vibrational correction; the 'compression' values are those quoted by Tosi[2] who employed the compression ξ . Conclusions similar to those for the Na and K halides[1] apply here, with the additional observation that in the Rb sequence $d_0/\rho = n+1$ is precisely linear with d_0 . It was in this connection that the new value of the RbF lattice constant was important. Linearity was nearly, but not precisely, found in the previous two sequences.

The quantity dB_T/dP vs. the ultrasonic Hildebrand repulsive parameter is shown in Fig. 3 for all three halide sequences. The different halides are not distinguished because they read uniformly from left to right, F-Cl-Br-I, in all three sequences (which would not have been the case had compression based parameters been used). It is seen that the twelve data are practically invariant at a common value of 5.5, a remarkable result. Close inspection shows a small slope in each sequence which, further, decreases systematically in the order Na, K, Rb.

The Born model in the power law version leads to the simple result, $dB_T/dP = (n+7)/3$. In deriving this expression vibrational terms have been omitted, but it can be shown that, if included, they largely cancel, leaving a small residue of around +3 per cent. Figure 3 shows that this expression gives the general

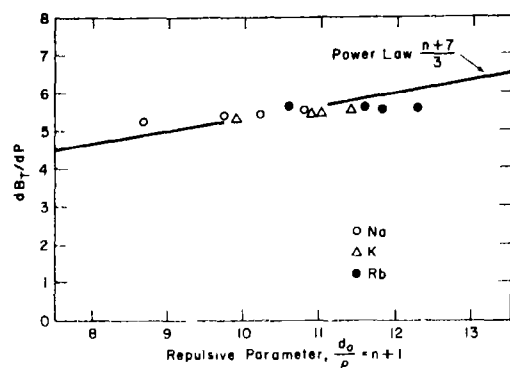


Fig. 3. Ultrasonic dB_T/dP at 295°K for the sodium, potassium and rubidium halides vs. repulsive parameter $d_0/\rho \sim n+1$. The members of each sequence occur monotonically from left to right in the order F, Cl, Br, I. The solid line is the prediction of the Born model in the repulsive power law version.

magnitude of dB_T/dP quite satisfactorily, but that the slope is too large. The exponential version of this expression yields the same slope for practical purposes, but magnitudes approximately 10 per cent lower and hence not in quite as good agreement with the facts as the power law version.

Acknowledgement—The research was supported by the AEC. Equipment was provided by ARPA.

REFERENCES

1. ROBERTS R. W. and SMITH C. S., *J. Phys. Chem. Solids* **31**, 619 (1970).
2. TOSI M. P., *Solid State Physics* (Edited by F. Seitz and D. Turnbull), Vol. 16, p. 1. Academic Press, New York (1964).
3. HENGLEIN F. A., *Z. Electrochem.* **31**, 424 (1925).
4. HAUSSUHL H., *Z. Phys.* **159**, 223 (1960).
5. SWENSON C. A., *J. Phys. Chem. Solids* **29**, 1337 (1968).

HALL STUDIES OF INSTABILITIES OCCURRING IN IMPACT IONIZATION OF *n*-TYPE INDIUM ANTIMONIDE

E. MÜLLER and D. K. FERRY

Department of Electrical Engineering, Texas Tech University, Lubbock, Texas 79409, U.S.A.

(Received 3 February 1970)

Abstract—The J - E characteristic of InSb shows an instability at short times after application of the electric field. A transverse magnetic field lets the instability occur at a lower electric field. The Hall field shows a sharp drop simultaneously to the instability. Carrier concentrations at the threshold field are measured for various magnetic fields.

1. INTRODUCTION

FOR TIMES of the order of microseconds after application of the electric field pulses, InSb exhibits an instability in the J - E characteristic [1, 2]. The threshold value for this instability lies at electric fields higher than those necessary for impact ionization, which occurs at fields of the order of 210 V/cm [3]. The application of a transverse magnetic field tends to drive the threshold of the instability to a lower electric field. The instability occurs under both constant-current and constant-voltage conditions at the same threshold value when measured for the same time after application of the electric field pulse. This instability in the J - E characteristic is accompanied by a sudden drop in the Hall field. After a longer time (50–200 nsec) after application of the electric field, the instability in the J - E characteristic dies out and the instability in the Hall field is replaced by a saturation of the Hall electric field.

Measurements of the instability in the J - E characteristic and its time dependence have been reported previously by Ancker-Johnson [1]. The influence of various magnetic fields on the J - E characteristic and the Hall field under constant-current conditions were reported earlier by Heinrich and Müller [4]. Hall measurements after longer times where the saturation of the Hall field with the electric

field shows up were reported by Toda and Glicksman [5]. Since the saturation in Hall field observed by these latter authors apparently occurred for an electric field below that necessary for avalanche breakdown, they interpreted their measurements as evidence of a transverse avalanche breakdown due to the Hall field. In these measurements, the Hall field was larger than the longitudinal electric field as the magnetic field was such that $\omega_c \tau = \mu B > 1$.

In the present paper, short time measurements of the instability are presented for an experimental configuration in which the sample is maintained in a constant voltage configuration. These measurements show that the instability which occurs in the J - E characteristic, and is reflected in the Hall electric field, occurs only after the carrier density is increased due to impact ionization. Further, the onset of the Hall field saturation, at long times which has been interpreted as transverse breakdown, occurs only after the instability dies out and only after impact ionization, due to the longitudinal electric field, has occurred.

2. EXPERIMENTAL ARRANGEMENT

All experiments are performed with the samples cooled to 77°K. The samples were prepared from slices of *n*-type InSb, of carrier concentrations $2 \times 10^{14} \text{ cm}^{-3}$ and carrier mo-

bility of $5 \times 10^5 \text{ cm}^2/\text{V-sec}$. The samples are cut in a bridge shape using a spark cutter. This method provides minimal mechanical damage to the bulk material. Typical sample dimensions are $0.3 \times 0.03 \times 0.01 \text{ cm}$. The probes which detect the voltages along the samples are high impedance probes and are monitored by a sampling oscilloscope. The samples are mounted in 50Ω insertion unit. The electric field pulse is provided by a transmission line discharge pulser. Great care is taken to maintain the impedance as close to 50Ω as possible throughout the entire experimental apparatus. The voltages detected by the oscilloscopes are plotted by an X-Y recorder. Figure 1 shows the experimental arrangement.

curves of current density as a function of the electric field are shown in Fig. 2. These curves were measured at a time of 5 nsec after application of the electric field.

Hall measurements taken simultaneously with the J - E characteristic show a very close connection to this instability. The Hall field increases with increasing electric field up to the value at which the unstable behavior in the current density occurs. At this value, a sudden drop in the Hall field occurs. This is shown in Fig. 3. The magnetic field is the parameter for these curves. All curves were measured at a time of 5 nsec after application of the electric field.

For one particular magnetic field the characteristic does not change very significantly

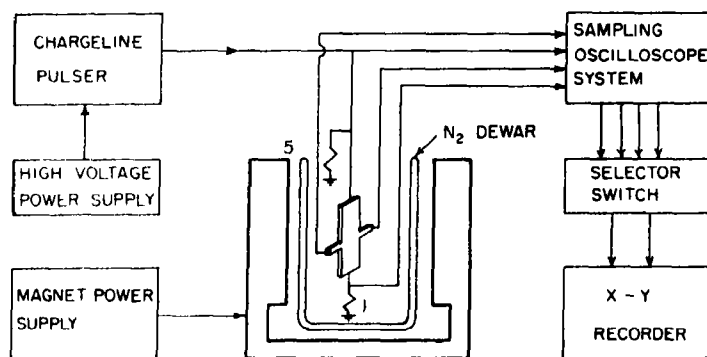


Fig. 1 Experimental arrangement.

3. EXPERIMENTAL RESULTS

The instability of the J - E characteristic manifests itself, under constant-voltage conditions, as a sudden increase of the current density at a constant electric field. This instability occurs between times of 2.5 nsec and about 50 nsec after application of the electric field pulse. Application of a transverse magnetic field causes the instability to occur at a lower longitudinal electric field. However, the threshold never decreases to values of the electric field lower than the values for which impact ionization occurs. Typical

with the time after application of the electric field. This is shown in Fig. 4 and Fig. 5, which display the corresponding curves for the J - E characteristics and Hall field, respectively, as a function of the longitudinal electric field. The electron densities for the electric fields just before the instability, have been calculated. The results are plotted as a function of the magnetic field in Fig. 6.

4. DISCUSSION

The measurements reported here show that the instability exists only for fields which

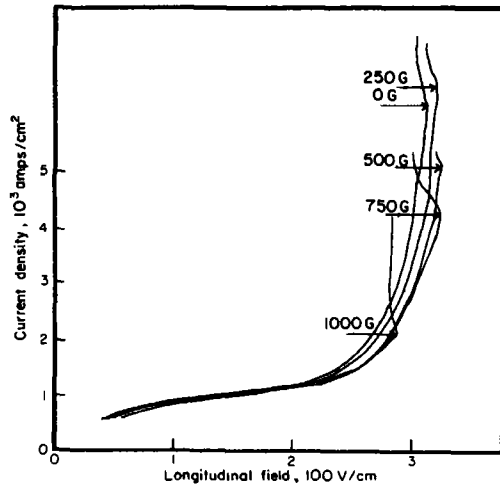


Fig. 2. Current density as a function of the longitudinal electric field at different transverse magnetic fields at a time of 5 nsec after application of the electric pulse.

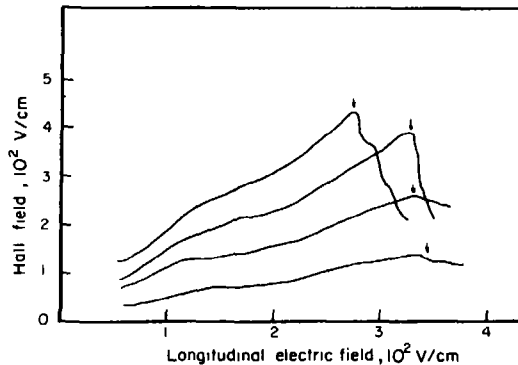


Fig. 3. Hall field as a function of the longitudinal electric field for different values of the transverse magnetic field at a time of 5 nsec after application of the electric pulse. The arrows denote the onset of the instability.

are strong enough to cause impact ionization in the longitudinal direction. From measurements of the time dependence of the instability at various side-arms along the sample, for constant-current conditions, the onset of the instability shows a drift through the bulk material characterized by the drift velocity

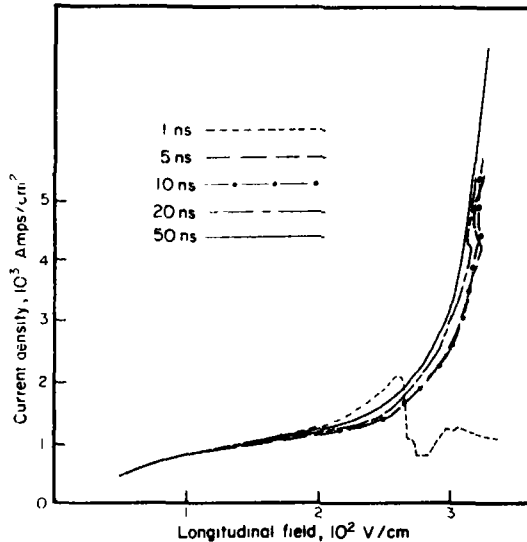


Fig. 4. Current density as a function of the longitudinal electric field at different times after application of the electric pulse at a transverse magnetic field of 750 G.

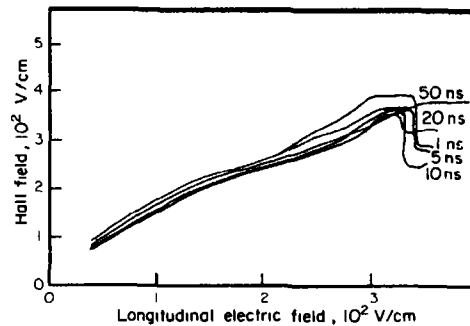


Fig. 5. The Hall field as a function of the longitudinal electric field for a transverse magnetic field of 750 G. The different curves correspond to different times after application of the electric pulse.

of the carriers. Under the constant voltage conditions used for this report, the instability shows no measurable velocity, but occurs instantaneously throughout the sample. This behavior agrees somewhat with a theory of negative differential resistance in bulk materials presented by Ridley[6]. For constant-

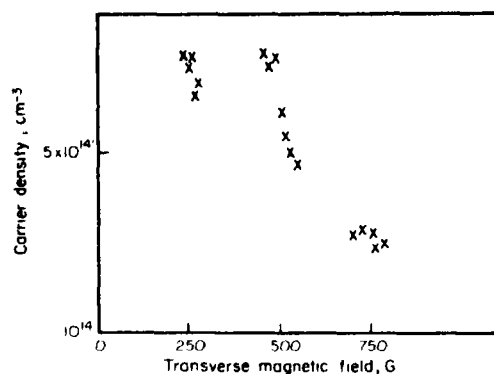


Fig. 6(a)

voltage conditions, the theory predicts the development of high-current filaments. This would cause the instability to occur over the entire sample simultaneously. It is possible that the instability is connected with this type of behavior. It is possible that instability is caused by the sharp increase in conductivity when impact ionization occurs, and disappears when the filamentary domains are formed.

REFERENCES

1. ANCKER-JOHNSON D., *J. phys. Soc. Japan* **22**, 1156 (1967)

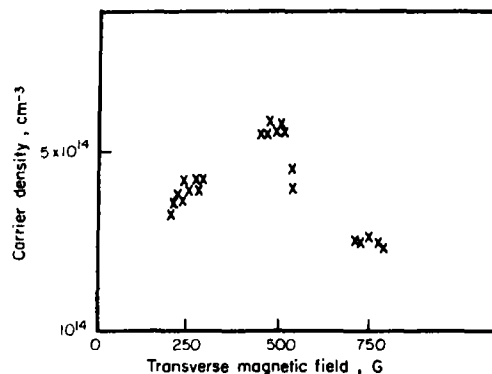


Fig. 6(b).

Fig. 6. (a) Carrier density at electric fields where the instability occurs as a function of the magnetic field at 5 nsec after application of the electric pulse. (b) Carrier density at electric fields where the instability occurs as a function of the magnetic field at 10 nsec after application of the electric pulse.

2. FERRY D. K. and HEINRICH H., *Phys. Rev.* **169**, 670 (1968)
3. GLICKSMAN M. and STEELE M. C., *Phys. Rev.* **110**, 1204 (1958).
4. HEINRICH H. and MÜLLER E., *Solid State Commun.* **6**, 391 (1968)
5. TODA M. and GLICKSMAN M., *Phys. Rev.* **140**, 1317 (1965)
6. RIDLEY B. K., *Proc. Phys. Soc.* **82**, 954 (1963).

EFFECT OF ELECTRON IRRADIATION ON LITHIUM-DOPED SILICON*

J. R. CARTER, Jr.

TRW Systems Group, Redondo Beach, Calif. 90278, U.S.A.

(Received 13 October 1969; in revised form 15 January 1970)

Abstract—Lithium-doped silicon was irradiated at room temperature with 1 MeV electrons. The initial carrier removal rate was 2.2 cm^{-1} in float zone silicon. As larger quantities of carriers were removed, the carrier concentration varied exponentially with electron fluence. The changes in Hall coefficient after irradiation indicate that lithium is consumed in the production of defects. Changes in Hall mobility in float zone silicon indicate production of a neutral defect which consumes one conduction electron for each lithium atom reacting. In quartz crucible silicon, a different neutral defect results after intermediate Si-A center formation. Similar measurements in phosphorus-doped float zone silicon indicate the formation of negatively charged defects which appear to be silicon E' -centers.

1. INTRODUCTION

RECENT interest in the use of lithium doping in silicon devices to achieve radiation hardness [1, 2] suggests the need for more basic data regarding the nature of displacement damage in lithium-doped silicon. Earlier work by Vavilov *et al.* [3] was confined to quartz crucible grown silicon. A more recent study on floating zone grown silicon involved lithium doping during crystal growth [4]. The efforts reported here involve similar studies in silicon doped by diffusion of lithium into the samples. Vavilov's work suggested that defects with an $E_c-0.17 \text{ eV}$ level ('A' centers) were formed during irradiation. The lithium ions then slowly reacted with $E_c-0.17 \text{ eV}$ level defects to neutralize them. The results in Ref. [4] also indicated a time-dependent second step after the irradiation, but failed to detect the presence of $E_c-0.17 \text{ eV}$ level defects. In the work on float zone silicon reported herein the oxygen concentration was low and the lithium concentrations relatively high to limit possible interactions.

2. EXPERIMENTAL

The 1 MeV electron irradiations were done at 27°C with the TRW Systems Group 1 MeV Van de Graaff. The electron flux rate was approximately $3 \times 10^{15} \text{ e/cm}^2\text{-hr}$. The float zone silicon used was manufactured by Dow Corning and had a resistivity of about $75 \Omega\text{-cm}$. The lithium was diffused into the silicon at 600°C from a LiAlH_4 solution source. The wafers were cleaned and allowed to equilibrate at a lower temperature. The wafers were ultrasonically machined into six-armed bridge specimens for Hall measurements. Electroless nickel plated contacts on the specimen arms allowed attachment of electrical leads. In this manner samples have been prepared with lithium donor concentrations between 10^{16} and $10^{18} \text{ atoms/cm}^3$. Table I summarizes the various electrical properties of the samples prepared. The electrical properties of this material are typical of phosphorus or arsenic-doped silicon in regard to Hall mobility and Hall coefficient. In all cases the mobility found in the lithium-doped specimens was very close to the published experimental and computed values of Morin and Maita for arsenic-doped silicon [5]. This would indicate that the scattering centers are singly charged lithium donor atoms.

*Work supported by Jet Propulsion Laboratory Contract No. 952251.

Table 1. Properties of Li diffused silicon specimens

Sample No.	Silicon	Li diffusion	$\rho(\Omega\text{-cm})$	$R(\text{cm}^3/\text{C})$	$\mu_H(\text{cm}^2/\text{V-sec})$	Li(atoms/cm ³)
B-1	75 $\Omega\text{-cm}$, n, F. Z.	1 hr @ 600°C	0.012	2.18×10^0	180	3.4×10^{18}
D-2	75 $\Omega\text{-cm}$, n, F. Z.	1 hr @ 600°C, 8 hr @ 200°C	0.078	6.35×10^1	815	1.2×10^{17}
A-1	75 $\Omega\text{-cm}$, n, F. Z.	1 hr @ 600°C 60 hrs @ 200°C	0.26	2.72×10^2	1150	2.7×10^{16}
C-1	75 $\Omega\text{-cm}$, n, F. Z.	1 hr @ 600°C 48 hrs @ 150°C	0.50	6.32×10^2	1280	1.6×10^{16}
Q-1	50 $\Omega\text{-cm}$, n, Q. C.	1 hr @ 600°C 60 hrs @ 200°C	0.12	1.10×10^2	935	6.7×10^{16}

3. RESULTS AND DISCUSSION

Most of the studies of irradiation carrier removal and defect production in silicon have either confirmed or assumed a linear change in radiation defect population with increasing electron fluence. One exception occurs when the Fermi level lies close to ionization level of the radiation defect. In this case the removal rate changes rapidly as the Fermi level crosses the defect ionization level. This occurrence has been proposed as a method of determining defect energy levels[6]. The early work by Wertheim demonstrated that carrier removal is linear at low electron fluences, but as defect concentration approaches the original impurity concentration, the rate becomes nonlinear [7]. Since the production of a defect complex often involves the consumption of a donor, a rapid decrease in the introduction rate should occur as its constituent impurity is near exhaustion. In this work lithium-doped silicon was studied by observing changes in the removal rate as a function of electron fluence. In this manner some information can be obtained regarding structure of radiation defects.

The electron irradiation results for this float zone silicon are shown in Fig. 1. Sample D-2, described in Table 1, was irradiated in increments with 1 MeV electrons at room temperature. When the irradiation was interrupted, the resistivity and Hall coefficient were determined. The electron carrier concentration, as determined by the Hall coefficient, is plotted as a function of electron fluence.

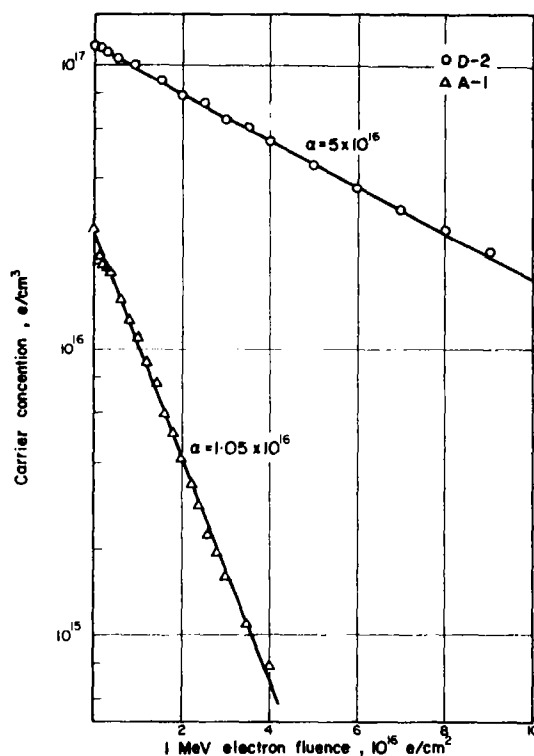


Fig. 1. Carrier removal, lithium doped F. Z. silicon.

Since the logarithm of the carrier concentration vs. fluence yields a straight line, it appears that this material has demonstrated the same exponential dependence of carrier concentration upon electron fluence which was previously found in float zone silicon doped with lithium in the melt[4]. The results of these

irradiations are described by the following equation:

$$n = n_0 \exp(-\phi/\alpha)$$

where: n_0 = initial electron concentration

ϕ = electron fluence

α = a constant

n = electron concentration after irradiation.

Such a relationship indicates that the instantaneous removal rate ($dn/d\phi$) is not a constant, as has been found in other cases, but is directly related to the instantaneous carrier concentration (i.e. lithium donor concentration) as follows:

$$\frac{dn}{d\phi} = -\frac{n}{\alpha}$$

In the case of sample *D-2* the constant $\alpha = 5 \times 10^{16} \text{ e/cm}^2$. The exponential relation was found in all samples studied. The irradiation of a similar sample, with a lower lithium concentration, is shown in Fig. 1. In this case the constant α equals $1.05 \times 10^{18} \text{ e/cm}^2$. The appearance of an exponential removal is in no way in conflict with previously published work indicating linear removal. Because of the mathematical similarities between linear and exponential functions, the two behaviors can not be distinguished during small initial changes in carrier concentration. The constant α varied considerably in the four specimens studied. An empirical relationship observed between the initial carrier electron concentration and the values of the removal constant α appears to be:

$$\alpha = n_0/2.2 \text{ cm}^{-2}.$$

If this relationship is substituted into the instantaneous carrier concentration expression, the following expression results:

$$\frac{dn}{d\phi} = -2.2 \frac{n}{n_0}$$

This would result in:

$$\frac{dn}{d\phi} = -2.2 \text{ cm}^{-1}$$

at the start of irradiation when $n = n_0$. The physical reasons for this relationship are not apparent at this time. If, as one might expect, α was independent of lithium concentration, and the value of α found for a 10^{16} Li/cm^2 were to apply for samples of 10^{17} Li/cm^3 and greater, the value of $dn/d\phi$ would initially exceed that of the displacement rate for 1 MeV electrons. Such a situation would be very difficult to account for theoretically. The value of the initial removal rate found here ($2.2/\text{cm}$) is roughly equal to the calculated displacement rate of 1 MeV electrons in silicon[8]. The Hall coefficient of lithium doped silicon was examined as a function of temperature to investigate the nature of the defects generated by the irradiation. This type of data is shown in Fig. 2 for sample *A-1*, before and after irradiation. The predominant change after irradiation is a reduction in the reciprocal Hall coefficient at all temperatures. These results indicate that the loss in carrier electrons is caused largely by the formation deep acceptor or neutral defect-lithium complexes. If the defects are acceptor type, the energy level must be greater than 0.3 eV from bottom of the conduction band.

Sample *A-1* was irradiated with $4 \times 10^{16} \text{ e/cm}^2$ and isochronally annealed for 15 minutes at 75°C and higher temperatures at 25°C intervals. The annealing data for sample *A-1* is shown in Fig. 3. In the vicinity of 100°C about 10 per cent of the carrier removal damage is recovered. At 200°C what appears to be a second annealing stage begins. After annealing for 15 min at 275°C the carrier concentration has increased to approximately the same value found in the specimen prior to irradiation. Isochronal annealing at temperatures above 275°C produced rather startling results. Each successive annealing step increased the carrier concentration. After the anneal at 350°C the carrier concentration was five times greater than that found prior

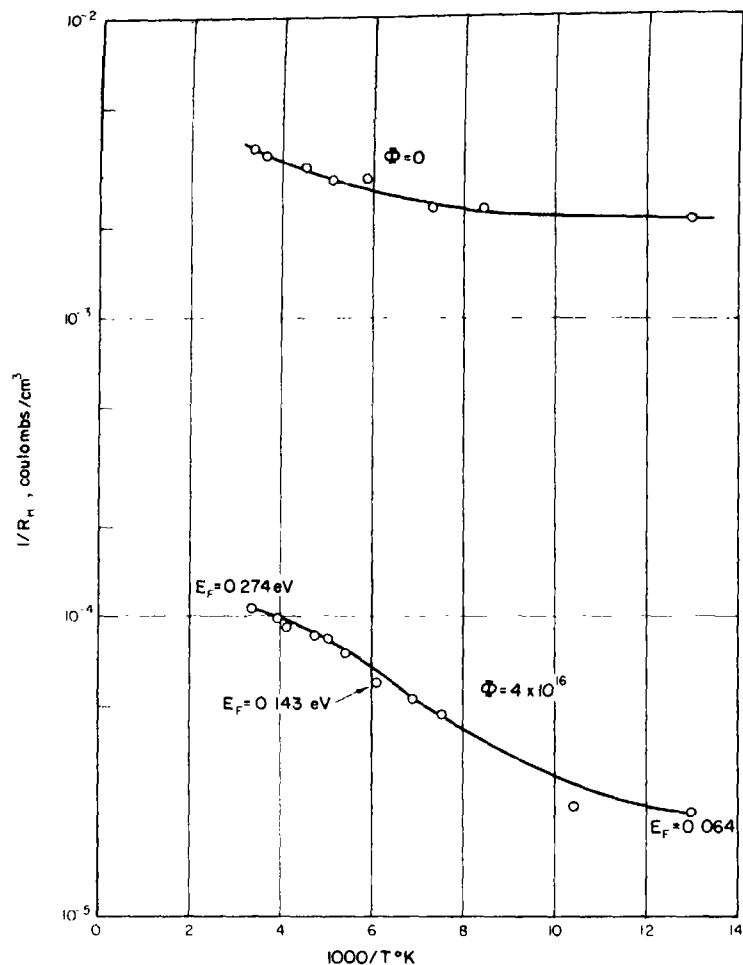


Fig. 2. Hall coefficient changes during irradiation, lithium doped F. Z. silicon.

to irradiation. The apparent explanation of this behavior lies in the comparison of the isochronal annealing data to the lithium solubility data of Pell, which is also plotted in Fig. 3[9]. Since the specimen was originally saturated with lithium at 600°C and then held at 200°C, the lower temperature produced a precipitated second phase of lithium silicide rather than outdiffusion of lithium as expected. The annealing above 200°C allowed the silicon to redissolve the precipitate, with subsequent increase of lithium donor concentration. The

annealing data show a tendency to approach the solubility data as temperature increases. The annealing data for sample D-2 is also shown on Fig. 3. The results are very similar to those just discussed, in that an annealing stage occurs near 100°C, redissolution occurs when the solubility of lithium at the annealing temperature exceeds the concentration of lithium previously detected in the specimen, and the concentration of Li present after the highest temperature anneal exceeded that initially present before the irradiation. If

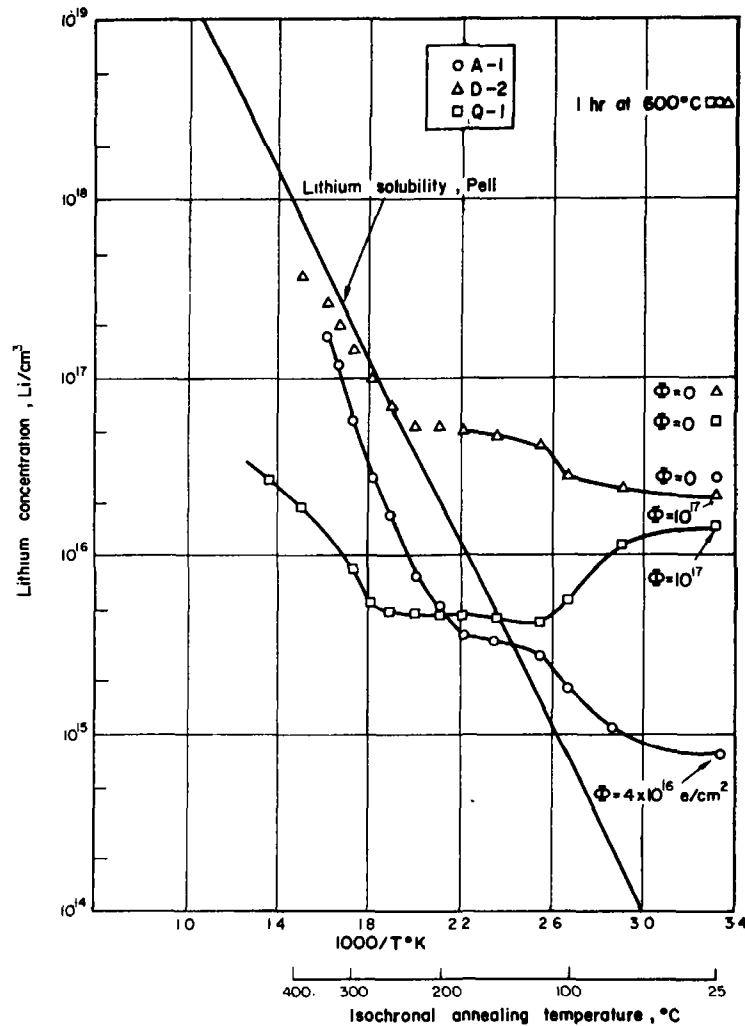


Fig. 3. Annealing of irradiated lithium doped silicon.

the observed effect is indeed lithium redissolving, it may mask the annealing of the remaining fraction of removal damage after annealing at 175°C . Further work is necessary to clarify these effects.

A second view of the irradiation of sample A-1 can be seen in Fig. 4. In this figure the Hall mobility of the specimen is plotted vs. the lithium donor concentration after several irradiations. In addition to the data points,

the arsenic data of Morin and Maita is shown as a solid line[5]. It can be seen that the irradiation of this sample results in an increase in the Hall mobility in addition to the loss of lithium donors. Even after an irradiation of $4 \times 10^{16} \text{ e}/\text{cm}^2$ the Hall mobility is equal to that of an unirradiated sample of the same donor concentration. Since Hall mobility increased, the irradiation results in no additional charge scattering centers, but rather a

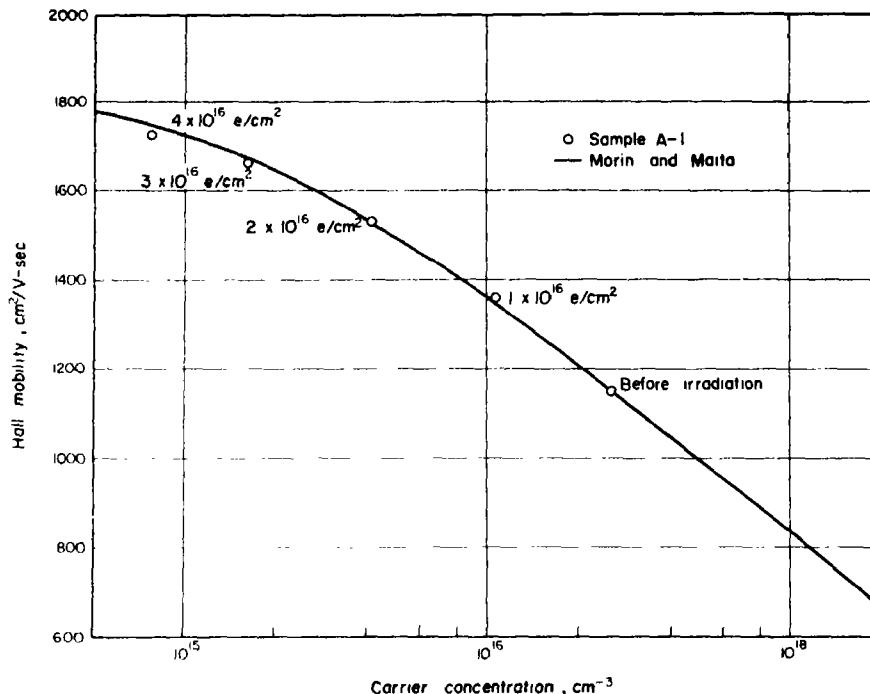


Fig. 4. Mobility changes during irradiation, lithium doped F. Z. silicon.

reduction of charged scattering centers. This condition rules out the production of charged acceptor type defects by the irradiation. Thus the irradiation appears to electrically resemble the precipitation process. Annealing had the exact opposite effect as irradiation, as each higher temperature increased the donor concentration and decreased the Hall mobility. Some of the major defect reactions which are known or hypothesized in *n*-type silicon are presented in Table 2. An examination of the table indicates that reactions 1 or 4 will cause the necessary changes in the population of carrier electrons and scattering centers to produce the observed changes in Hall coefficient and Hall mobility. Reaction 4 is actually the sum of reactions 2 and 3. Since reactions 2 and 3 have already been proposed as the degradation and recovery process in lithium doped solar cells, the assumption of reaction 4 or 2 + 3 presents an explanation of the Hall

measurement results which is consistent with the observations on irradiated devices[10]. In the cells, reaction 3 proceeds much slower than reaction 2 because of the lower lithium concentrations. Since the time constant of reaction 3 is decreased by the presence of a greater lithium concentration, it is possible that the lithium concentration is sufficient to allow completion during the irradiation of specimens described in this paper. The results of the irradiation are electrically similar to precipitation of lithium, although formation of a second phase is not indicated. In this respect the results confirm similar work in Li drifted junctions[11].

In a recent study reported by Stannard [12], an electron irradiation of lithium doped float zone silicon at low temperature was followed by an anneal at 300°K. The irradiation produced an acceptor of undetermined structure. The anneal resulted in the loss of

Table 2. Radiation defect production in n-type silicon

	Defect reaction	Change in conduction electrons	Change in scattering centers	Nature of defect
1.	$V + Li^+ + e^- \rightarrow Li-V^0$	Lose one	Lose one	Shallow acceptor, deep donor, or neutral defect
2.	$V + Li^+ + 2e^- \rightarrow Li-V^-$	Lose two	No change	Deep acceptor
3.	$Li-V^- + Li^+ \rightarrow Li-V-Li$	No change	Lose two	Neutral (inactive)
4. (2+3)	$V + 2Li^+ + 2e^- \rightarrow Li-V-Li$	Lose two	Lose two	Neutral (inactive)
5.	$O + V \rightarrow O-V^0$	No change	No change	Deep acceptor, un-ionized, ('A' center)
6.	$O-V^0 + e^- + Li^+ \rightarrow Li-O-V^0$	Lose one	Lose one	Neutral (inactive)
7. (5+6)	$O + V + e^- + Li^+ \rightarrow Li-O-V^0$	Lose one	Lose one	Neutral (inactive)
8.	$O + V + e^- \rightarrow O-V^-$	Lose one	Gain one	Deep acceptor, ionized ('A' center)
9.	$O-V^- + Li^+ \rightarrow Li-O-V^0$	No change	Lose two	Neutral (inactive)
10. (8+9)	$O + V + e^- + Li^+ \rightarrow Li-O-V^0$	Lose one	Lose one	Neutral (inactive)
11.	$V + LiO^+ + e^- \rightarrow Li-O-V^0$	Lose one	Lose one	Neutral (inactive)
12.	$V + P^+ + 2e^- \rightarrow P-V^-$	Lose two	No change	Deep acceptor ('E' center)

the radiation-produced acceptors and a loss of lithium donors. The net result of the irradiation and room temperature anneal was the loss of lithium donors, which is in agreement with the experimental results reported here. Stannard's results suggest that two lithium donors are lost in the annihilation of the radiation-produced acceptor. Such behavior may require an adjustment of the simple model presented here to allow the reaction of two lithium donors with the acceptor defect in reaction 3 to form a Li_3V neutral complex.

Quartz-crucible silicon was also lithium diffused and fabricated into a Hall specimen. The initial data for this sample is included in Table 1. The electron irradiation results of this sample (Q-1) differ somewhat from that of the float zone silicon. The removal constant α , for the lithium-doped Q.C. silicon, was roughly twice the value found for float zone silicon of similar lithium concentration. The isochronal annealing after irradiation of sample Q-1, shown in Fig. 3, produced a significant decrease in the carrier or lithium donor concentration in the 75–100°C range. This behavior is in marked contrast to that observed in annealing of irradiated, float zone, lithium-doped silicon. The decrease or 'reverse anneal' observed in sample Q-1 reduces the carrier concentration present after irradiation by about 50 per cent. This change

represents a roughly 25 per cent increase in number of carriers removed during the irradiation. An additional experimental result supports the need for a different damage model for quartz crucible silicon as opposed to that used for float zone silicon. Fig. 3 shows that the final defect complex in sample Q-1 does not begin to anneal until temperatures of 300°C are reached. The defect complexes in the float zone samples anneal at much lower temperatures.

The experimental results of room temperature Hall mobility measurements during the irradiation and annealing of sample Q-1 are presented in Fig. 5. The initial behavior of sample Q-1 during irradiation can be characterized by a loss of conduction electrons and an equal loss of charge scattering centers (increase in Hall mobility). After the electron fluence of roughly $5 \times 10^{16} \text{ e/cm}^2$, the conduction electron concentration continued to decrease during irradiation, but the Hall mobility changes indicated that the scattering center concentration was not decreasing at the same rate.

The behavior of sample Q-1 requires a different model than that used to explain behavior in float zone lithium cells and bulk silicon. The early work of Vavilov *et al.* [3], suggested that during the irradiation of lithium-doped quartz crucible silicon, oxygen-

vacancy pairs (Si-A centers) with a $E_c - 0.17$ eV energy level and other defects with shallower energy levels were formed. The oxygen concentration in the quartz-crucible silicon is approximately $5 \times 10^{17} \text{ cm}^{-3}$. This value is much larger than the concentration of lithium in sample Q-1. Pell has shown that in such a sample most of the lithium reacts to form lithium-oxygen donor pairs[8]. In the case of sample Q-1, the oxygen concentration will be large compared with that of the lithium-oxygen donor pairs. During irradiation, the displacement products can react with the higher concentrations of oxygen atoms to form 'A' centers or with less common lithium-oxygen pairs to form some undetermined defect complex. The initial Fermi level in sample Q-1 is 0.16 eV below the conduction band. This means that if 'A' centers are formed during the irradiation, those formed at the start of the irradiation will be roughly 80 per cent ionized and those formed at the end of the 10^{17} e/cm^2 irradiation will be roughly 40 per cent ionized. For this reason any proposed model for the damage in quartz crucible silicon must examine the behavior of the 'A' center acceptor in both charge states.

Reaction 5 in Table 2 illustrates the formation of an un-ionized 'A' center. This reaction does not change the concentration of conduction electron or scattering centers. Reaction 6 illustrates the reaction of a lithium donor with the un-ionized 'A' center to form an inactive defect. Such a reaction of an uncharged 'A' center with a lithium donor causes an equal loss of carrier electrons and scattering centers. The sum of the reactions 5 and 6 (reaction 7) also produces an equal loss of conduction electrons and scattering centers. Reactions 8-10 of Table 2 illustrate the comparable reactions for an ionized 'A' center. Although the total reaction (10) for the ionized 'A' center produces the same electrical results as that for an un-ionized 'A' center, an important difference occurs when the reaction remains incomplete. When an ionized

'A' center is produced during irradiation (reaction 8), one conduction electron is lost and an additional scattering center is generated. If some of these scattering centers remain without reacting with lithium donors, the Hall mobility must fall below that shown by the solid line on Fig. 5. When the ionized 'A' center reacts with a lithium donor (reaction 9) the additional scattering centers will disappear with no change of carrier concentration. In the similar reaction of an un-ionized 'A' center (reaction 6) results in loss of both a conduction electron and a scattering center.

The behavior shown in Fig. 5 can be explained as follows. During first $5 \times 10^{16} \text{ e/cm}^2$ of fluence the behavior can be explained by the formation of inactive complexes which eliminate one conduction electron and one scattering center per complex. Either reaction 7, 10, or 11 will produce this effect. Since the end product is the same in all cases (a Li-O-V complex), the selection of the specific reaction route is of little importance during the early irradiation. It should be noted that 80 per cent of any 'A' centers formed will be ionized, favoring reaction 10 (8+9) over 7 (5+6) at this point. The negative charge on such 'A' centers should provide a coulombic attraction for the lithium donor necessary for reaction 9. During the final portion of the irradiation roughly 50 per cent of any 'A' centers present will be ionized, and the progress of reactions 6 and 9 have slowed because of the reduced lithium donor concentration. The presence of some ionized 'A' centers reduces the Hall mobility to a value lower than that due to lithium and lithium-oxygen donors alone. During the isochronal anneals at 75, 100 and 125°C, increased concentrations of lithium donors became available for reactions 6 and 9 through the thermal dissolution of lithium-oxygen donors. These annealing cycles allow reactions 6 and 9 to go to completion. The annihilation of the ionized fraction of the 'A' centers reduces the scattering center

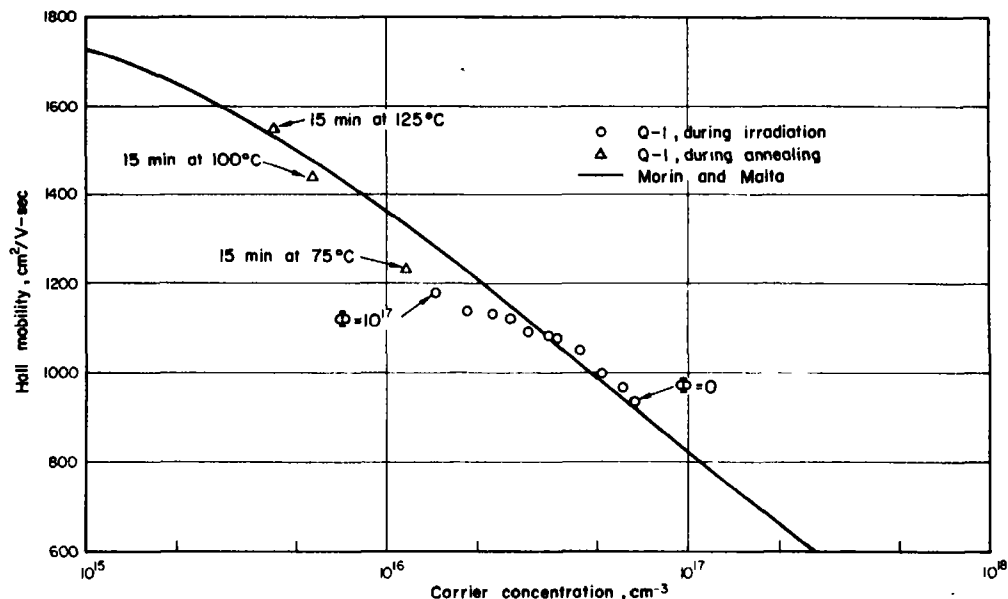


Fig. 5. Mobility changes during irradiation and annealing, lithium doped Q. C. silicon.

population to that of only the lithium or lithium-oxygen donors remaining. The annihilation of the un-ionized fraction of remaining 'A' centers will cause an additional loss of conduction electrons and an equal loss of scattering centers. As a result of the completion of these reactions the Hall mobility of sample Q-1, after 15 min at 125°C, is very close to the value indicated by the solid line in Fig. 5.

Since the irradiation of lithium-doped float zone silicon is mainly a relatively simple interaction of donors with the displacement products, it is interesting to compare the behavior with that of phosphorus-doped float zone silicon. Although considerable work has been done on phosphorus-doped silicon, most of the data reported relates to more lightly doped material than that considered in the lithium studies reported here. To make comparative studies, two samples of phosphorus-doped float zone silicon were obtained. The starting resistivities were roughly 0.1 and 0.2 Ω -cm. These resistivities

were selected to maximize the population of phosphorus over oxygen, without reaching resistivities which require unreasonably large electron fluences to cause the desired carrier removal. The previous investigations [13] have shown that *E*-centers (a phosphorus-vacancy pair, acceptor) and *A*-centers (an oxygen-vacancy pair, acceptor) are the most likely defects to form in irradiated silicon of this type.

The changes in carrier concentration during electron irradiation were monitored by Hall measurements. The results are shown in Fig. 6. It can be seen that the carrier removal in these samples also tends to follow the exponential behavior observed for lithium-doped silicon. The general trend indicates that in this material $\alpha = n_0$, the initial concentration of phosphorus before irradiation, whereas in the lithium doped material $\alpha = 0.45 n_0$. The Hall mobility data from the above study is shown in Fig. 7. The mobility values before irradiation are very close to the values published for unirradiated silicon. In the case

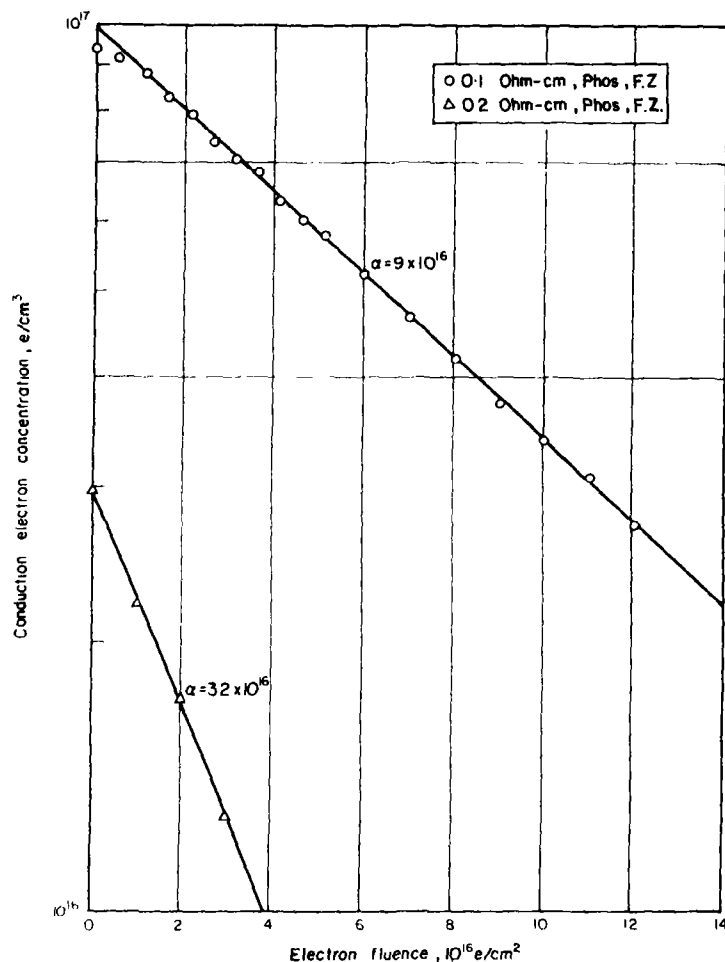


Fig. 6 Carrier removal, phosphorus doped F. Z. silicon

of both phosphorus-doped samples, the increasing electron fluence reduces the carrier concentration, but does not change the mobility. This result is in marked contrast to that found in lithium-doped float zone silicon, as shown in Fig. 4. The behavior observed in Fig. 7 can most easily be explained by assuming that reaction 12 causes the loss of carrier electrons and no net changes in the scattering center population. Such a reaction will produce no change in the Hall mobility. If only ionized *A*-centers are formed during

irradiation (reaction 8), the mobility will decline. Since no change in mobility is observed, it can be concluded that all the behavior can be explained by the formation only *E*-centers and no *A*-centers.

The relationships between α and n_0 indicate that carrier removal rates in lithium-doped float zone silicon are roughly twice those found in the phosphorus doped material. Since both reactions 4 and 12 cause the loss of two carrier electrons per reacting vacancy, the removal data indicates that twice as many

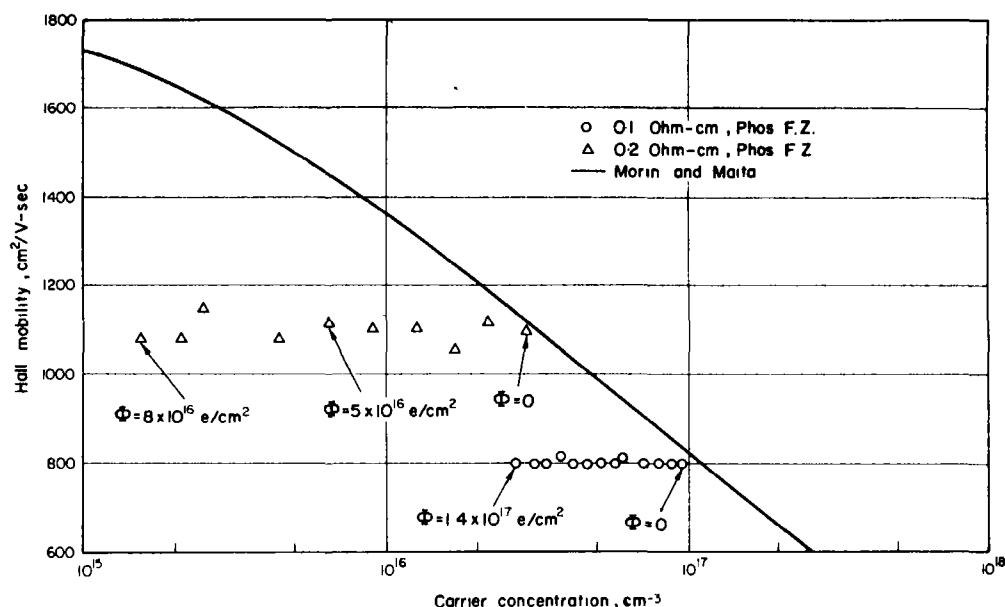


Fig. 7. Mobility changes during irradiation phosphorus doped F. Z. silicon.

vacancies are captured by lithium atoms before annihilation compared to a similar concentration of phosphorus atoms in silicon.

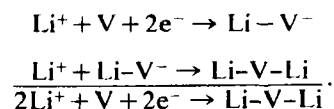
The following conclusions can be drawn from the experimental results:

1. The carrier removal rate for electron irradiation of lithium-doped float zone silicon is an exponential function of electron fluence.

2. During the initial stages of irradiation the removal rate is 2.2 cm^{-1} for the above described material.

3. The damage process in heavily lithium-doped floating zone silicon consists of the loss of the carrier electrons with an equal loss of charge scattering centers.

4. The best available atomistic model to describe the damage is the following series reaction:



The reaction of $\text{Li}^+ + \text{V} + \text{e}^- \rightarrow \text{LiV}^0$ will also describe the observed behavior, but is inconsistent with the observed production and annihilation of recombination centers in lithium-doped solar cells.

5. The isochronal annealing in float zone silicon is characterized by a low temperature partial anneal in the $75\text{--}100^\circ\text{C}$ range and re-solution of lithium at higher temperatures.

6. The irradiation of lithium-doped quartz-crucible silicon results in a tendency to form a different neutral defect complex. Silicon 'A' centers may be formed as an intermediate stage in this process. After very long irradiations, some Si-A centers may remain unneutralized because of lack of available lithium donors and kinetic limitations. Low temperature annealing allows the reaction to go to completion.

7. In similar floating zone silicon doped with phosphorus rather than lithium, the damage can be described by the formation of E-centers.

REFERENCES

1. VAVILOV V. S., *Radiation Damage in Semiconductors*, p. 115. Academic Press, New York (1964).
2. WYSOCKI J. J., *IEEE Trans. NS-13*, 168 (1966).
3. VAVILOV V. S., CHAPNIN V. A. and Smirnova I. V., *J. phys. Soc. Japan* **18**, 236 (1963).
4. CARTER J. R. Jr., *IEEE Trans. NS-14*, **6**, 110 (1967).
5. MORIN F. J. and MAITA J. P., *Phys. Rev.* **96**, 28 (1954).
6. FAN H. Y. and LARK-HOROVITZ K., *Report on the Conference Defects in Crystalline Solids*, Phys. Soc. London (1954).
7. WERTHEIM G. K., *Phys. Rev.* **105**, 1730 (1957).
8. CAHN J. H., *J. appl. Phys.* **30**, 1310 (1959).
9. PELL E. M., *Solid State Physics in Electronics and Telecommunications*, Vol. 1, p. 261. Academic Press, New York (1960).
10. WYSOCKI J. J., *Proc. 6th Photovoltaic Spec. Conf.* Vol. 3, p. 96 (1967).
11. AMMERLAAN C. A. J., *J. appl. Phys.* **39**, 6023 (1968).
12. STANNARD J. E., *Appl. Phys. Lett* **15**, 93 (1969).
13. WATKINS G. D., CORBETT J. W. and WALKER R. M., *J. appl. Phys.* **30**, 1198 (1959).

PHONON FREQUENCIES OF RARE EARTH TRICHLORIDES WITH UNIT CELLS OF DIFFERENT DIMENSIONS*

G. SCHAACK† and J. A. KONINGSTEIN

Department of Chemistry, Carleton University, Ottawa 1, Ontario, Canada

(Received 10 November 1969; in revised form 14 January 1970)

Abstract—The phonon Raman spectra of isomorphous single crystals of LaCl_3 , CeCl_3 , NdCl_3 , EuCl_3 and GdCl_3 have been investigated. GdCl_3 , the last in the series of hexagonal rare earth trichlorides, has a phonon spectrum, which differs markedly from the other spectra. The shift of the phonon frequencies with the decreasing volume of the unit cell for increasing atomic number (z) of the rare earth ions is discussed.

1. INTRODUCTION

THE ANHYDROUS *R.E.* chlorides form an isomorphous series of hexagonal crystals for the ions La to Gd. The space group of these lanthanide crystals is $C6_3m(C_{3h}^2)$. The structure of the crystals TbCl_3 and DyCl_3 is not known, but monoclinic crystals are found in the series starting by HoCl_3 and ending by LuCl_3 [1, 2]. The changes in structure are apparently related to a decreasing size of the rare earth ion as the atomic number increases (the radius of the La^{3+} ion is 1,061 Å; for Lu^{3+} ; $r = 0,848$ Å). As a result the phonon frequencies of the crystals are expected to shift with changing atomic number of the Lanthanide ions, but only because of the increase of the mass of the rare earth ions.

Recently information has become available [4–8] on the phonon spectra of some of the *R.E.* Chloride crystals. Good quality Raman spectra of the compounds CeCl_3 and PrCl_3 have been reported [3, 8, 11] and an analysis of the phonons and also of electronic Raman effects in these crystals have been made. Data are also available on the infrared spectra of the crystals LaCl_3 and PrCl_3 [7] and in this

communication the Raman spectra of the crystals NdCl_3 , EuCl_3 and GdCl_3 and additional data on LaCl_3 and CeCl_3 are reported.

2. RESULTS AND DISCUSSION

The hexagonal crystals of the rare earth chloride series contain two formula units in the elementary cell. The motions of the particles in the cell give rise to the following Raman active modes: three E_{2g} modes, two A_g modes and one E_{1g} mode.

Besides these there are three infrared active modes ($2 E_{1u}$, $1 A_{1u}$) and 5 'silent' modes ($2 B_u$, $2 B_g$, $1 E_{2u}$). The number of observed Raman transitions and their polarization properties are in agreement with the group theoretical predictions, however, as Satten *et al.* [6], observed, wandering of the optical axis and the divergence or convergence of light beams deteriorates very sensitively the depolarization ratios observed in these crystals.

The Raman spectra of single crystals of the rare earth chloride crystals reported were studied at various temperatures of the samples. A description of the experimental arrangement has been given elsewhere [9]. The 6328 Å radiation of the He–Ne laser and the 5145, 4880 and 4579 Å line of the Ar^+ laser were employed to excite the Raman spectra. The reason that these lines had to be employed

*Supported in part by grants from the National Research Council of Canada and the Defense Research Board.

†Permanent address: Institut für Technische Physik der Technischen Hochschule Darmstadt, Germany.

was that the crystals contained some (rare earth) impurities which cause, in nearly all cases, strong fluorescence. It was also observed that the scattered light of the crystals was absorbed at wavelengths where Raman transitions should occur. The Raman spectra of the compounds LaCl_3 and GdCl_3 are compared in Fig. 1 and the components of the scattering tensor for the latter crystal can be seen in Fig. 2. The spectra were studied from crystals measuring $10 \times 5 \times 3$ mm, they were cut from boules grown by the Stockbarger method. All samples were cut and polished along the (110) cleavage plane whenever possible and the orientation of the crystals was controlled by using a polarizing microscope. The spectrum of LaCl_3 shown in Fig. 1 is typical of all rare earth chloride crystals except that of GdCl_3 . The intensities and the frequencies of Raman lines of this crystal differ remarkably from the intensity

and frequencies of the other *R.E.* chloride crystals (see Fig. 1). The observed frequencies and the assignment of the Raman lines of a number of rare earth compounds are given in Table 1. The shifts of the phonon frequencies as a function of the atomic number of the lanthanide ions and also the relative variation of the unit cell volume is schematically given in Fig. 3. Although the change of the size of the unit cell appears to be quite smooth, this cannot be said about the change in the positions of the phonon frequencies and in particular the results of GdCl_3 are quite surprising. The Raman spectrum of this compound has been studied quite extensively and the crystallographic structure of the sample was investigated by means of X-ray diffraction measurements. The structure was hexagonal and complete agreement with previously published data were obtained [4].

The symmetry coordinates of the *R.E.* Chlorides have been constructed [4] and it appears that the rare earth ions participate only in movements of the crystal which give rise to Raman lines of symmetry E_{2g} . These motions of E_{2g} -symmetry of the lanthanide ions together with the motions of the chlorine

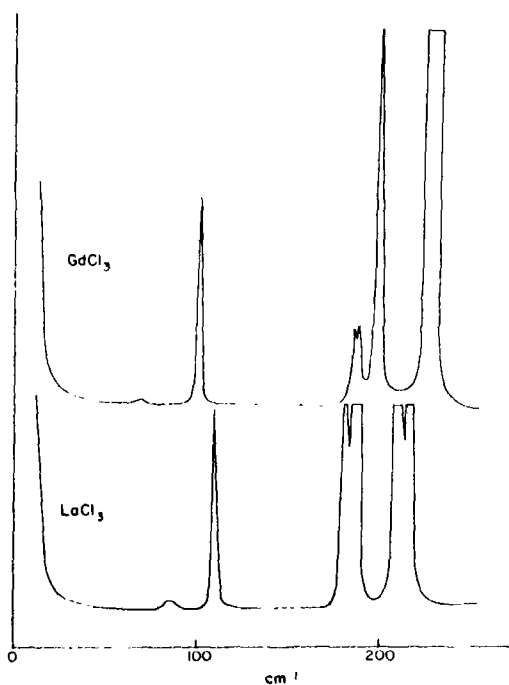


Fig. 1. Raman spectra of LaCl_3 and GdCl_3 , $T = 80^\circ\text{K}$. The figure shows a superposition of $z(yv)y$ and $z(yz)y$.

Table 1. Position of Raman shifts of *R.E.* Cl_3 crystals

		LaCl_3	CeCl_3	NdCl_3	EuCl_3	GdCl_3
300°K	E_{2g}		102			
	E_{2g}		178			
	A_g					
	E_{1g}		184			
	A_g		208			
80°K	E_{2g}		218			
	E_{2g}	108.0	108.4	103.6	107.5	99.3
	E_{2g}	179.8	183.1	183.5	180.3	193.2
	A_g	181.6				179.4
	E_{1g}	187.0	194.8	192.6	187.4	203.4
10°K	A_g	210.9	216.8	218.6	211.2	189.8
	E_{2g}	217.6	221.5	225.5	217.5	234.4
	E_{2g}		109.6		107.9	99.0
	E_{2g}		183.6		184.8	193.5
	A_g					
80°K	E_{1g}		196.5		191.8	203.7
	A_g		217.8		218.4	190.0
	E_{2g}		222.1		221.1	234.1
	E_{1g}	83	74	50 (?)	62	66
	E_{1g}					

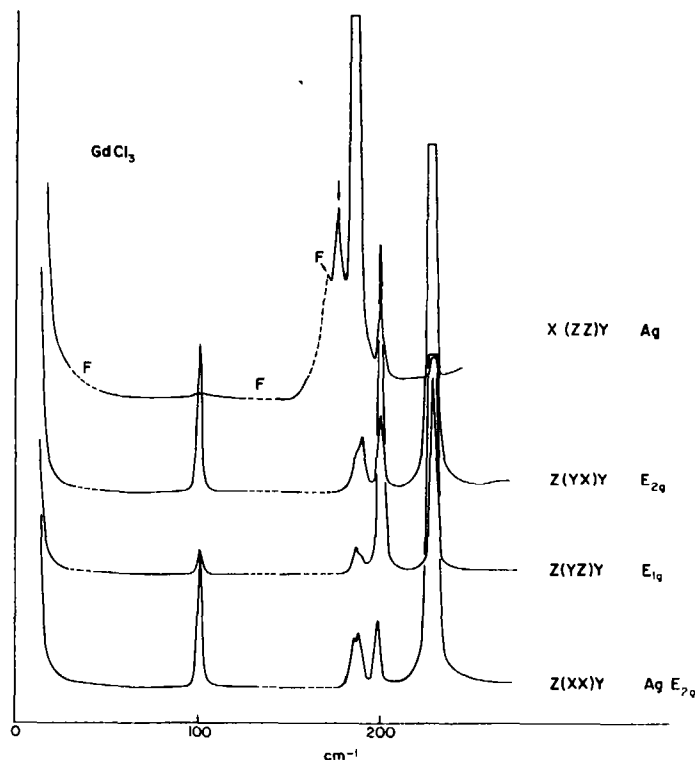
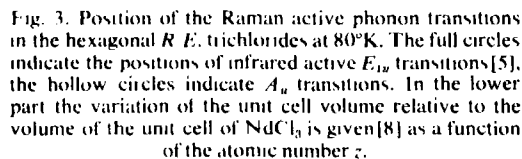


Fig. 2. Raman spectrum of GdCl_3 , $T = 80^\circ\text{K}$. The wave number regions indicated by broken lines were shaded by fluorescence bands.

ions are confined, however, in the (001) plane—the xy -plane of the crystal. The lowest lying E_{2g} level is expected to be related to translational motions of the complete $R.E. \text{Cl}_3$ groups. If the atomic number—thus the mass—of the lanthanide ions increases, then one expects a lowering of the frequency of this type of vibration. This is one part of the trend observed for the E_{2g} mode at $\sim 100 \text{ cm}^{-1}$ (see Fig. 3). The decrease of the volume of the unit cell has the opposite effect, the result of both is the complicated behaviour observed. The other two E_{2g} -modes react more sensitively on the volume decrease than on the mass increase. The A_g modes involve motions of only the Cl^- ions in the (xy) plane whilst the movements of these ions along the z -axis are labelled with the species E_{1g} . The fre-

quency changes of these modes are therefore solely determined by the contraction of the unit cell with increasing atomic number. An increase in the frequencies may be anticipated and the data of the crystals in the series of CeCl_3 to NdCl_3 are in agreement with the expectations. For EuCl_3 the trend is inverted and even more drastic changes occur for GdCl_3 . The latter compound is the last of the series with a hexagonal structure. Rare earth chloride crystals like TbCl_3 and others have a crystallographic structure of lower symmetry[10] than hexagonal. In interpretation of the drastic alterations of the Raman spectra in the series of CeCl_3 to GdCl_3 has to take this change of the structure into account.

Rare earth ions have low lying electronic levels and in the course of the investigation



All the crystals studied showed a broad Raman band with E_{1u} polarization in the low frequency region (see Table 1). Its intensity is more than one order of magnitude smaller than the intensity of the phonon modes

Kiel, *et al.* found[11] an excessive broadening, with increasing temperature, of the E_{1g} band at 196 cm^{-1} of CeCl_3 . As a possible interpretation they suggest a $4f$ -electron-phonon interaction. We have observed the same broadening of this line, while all other observed first order Raman lines of all compounds have a smaller width. They are instrumentally broadened and data on the actual line width of these modes are not available. So this broadening of the E_{1g} -mode in CeCl_3 seems to be the only indication of such an interaction, because the spectrum of a crystal with no $4f$ -levels (LaCl_3) at all or no levels in the investigated wavenumber region (EuCl_3) are very similar to the spectra of crystals with many electronic levels in the phonon region (CeCl_3 , PrCl_3 , NdCl_3).

Acknowledgements—The authors wish to thank Dr. J. Heber of the Institut für Technische Physik, T. H. Darmstadt, Germany, for growing some of the crystals used in the investigation, and to Dr. G. Y. Chao of the Geology Department of Carleton University for the X-ray investigation of the GdCl_3 crystal.

REFERENCES

1. ZACHARIASEN W. H., *J. chem. Phys.* **16**, 254 (1948).
2. TEMPLETON D. H. and DAUBEN C. H., *J. Am. chem. Soc.* **76**, 5237 (1954)
3. HOUGEN J. T. and SINGH S., *Proc. R. Soc. A*, **277**, 193 (1964).
4. MURPHY J., CASPERS K. H. and BUCHANAN R. A., *J. chem. Phys.* **40**, 743 (1964).
5. COHEN E. and MOOS H. W., *Phys. Rev.* **161**, 258, 268 (1967).
6. ASAWA C. K., SATTEN R. A. and STAFSUDD O. M., *Phys. Rev.* **168**, 957 (1968).
7. BERREMAN D. W. and UNTERWALD F. C., *Phys. Rev.* **174**, 797 (1968).
8. DAMEN T. C., KIEL A., PORTO S. P. S. and SINGH S., *Solid State Commun.* **6**, 677 (1968).
9. KONINGSTEIN J. A. and MORTENSEN O. S., *J. Molec. Spectrosc.* **27**, 343 (1968).
10. BOMMER H. and HOHMANN E., *Z. anorg. allg. Chem.* **248**, 373 (1941).
11. KIEL A., DAMEN T. C., PORTO S. P. S., SINGH S. and VARSANYI F., *Phys. Rev.* **178**, 1518 (1969).
12. CARLSON E. and DIEKE G. H., *J. chem. Phys.* **29**, 229 (1958).

THE EFFECT OF ALLOYING ADDITIONS OF PLUTONIUM AND NEPTUNIUM ON THE LATTICE PARAMETERS OF α -URANIUM BETWEEN 4 AND 300°K

J. A. C. MARPLES

Atomic Energy Research Establishment, Harwell, Berkshire, England

(Received 5 January 1970)

Abstract—The effect of plutonium and neptunium in solution on the thermal expansion anomaly in α -uranium at 43°K has been studied by X-rays. Both solutes reduce the size of the anomaly and the temperature at which it occurs. The results support the theory that the cause of the anomaly is inter-band transfer of electrons.

1. INTRODUCTION

THE NEGATIVE volume expansion coefficient in α -uranium below 43°K has been studied by various workers. Laquer[1] examined several polycrystalline specimens dilatometrically but his results were rather variable, probably due to preferred orientation. Bridge, Schwartz and Vaughn[2] used the X-ray powder method and, while their lattice parameters were not very accurate, showed that the anomaly was not due to a phase change. Barrett, Mueller and Hitterman[3] used a more elegant single crystal X-ray technique to investigate the variation with temperature of the individual lattice parameters. They found that a and b showed minima with negative expansion coefficients in these directions on cooling below 43°K. On the other hand, there was no minimum in the c -direction, the expansion coefficient actually increasing to a more positive value below 43°K. In addition these changes were correlated with variations in the atom position parameter y .

A dilatometric study by Hough, Marples, Mortimer and Lee[4] showed a volume expansion on cooling that agreed well with the X-ray results and also that it was possible to suppress the transformation by quenching. Andres[5] determined the principal expansion

coefficients between 1.5 and 10°K, by a capacitance technique and demonstrated that the electronic contributions to these were in the same ratio as the anomalous changes in lattice parameter between 0–43°K. Hence he deduced that the latter were due to changes in the cohesive energy of the electrons rather than to a lattice effect.

In addition papers have been published showing anomalies in Hall coefficient[6], elastic moduli[7,8], electrical resistivity [6, 9–11], magnetic susceptibility[12], specific heat[13] and thermal conductivity[14] at about 43°K. Geballe *et al.*[15] have sought to explain these anomalies and to relate them to the observed variation of superconducting critical temperature with pressure[16,17] and to the difference in T_c between single and poly-crystal specimens, on the hypothesis that, below 43°K, 0.04 electrons per atom were transferred from the conduction band to a localised, non-bonding $5f$ band. This would, (a) lead to an expansion of the lattice, the effective size of the atoms being increased and the strength of the bonding reduced and (b) inhibit the occurrence of superconductivity which is thought to be incompatible with the presence of f electrons. This electron transfer would be prevented by pressure

thus explaining the rapid rise of T_c with pressure. Further it is assumed that in polycrystalline specimens, anisotropic expansion leads to the generation of a pressure network in the grain boundaries which is responsible for the observed filamentary superconductivity.

In these circumstances it was thought that it would be useful to study the effect of alloying on the dilation anomaly. Plutonium [18] and neptunium [19] are the only elements which dissolve to any extent in α -uranium [20], the solubilities being about 10 per cent for plutonium and over 40 per cent for neptunium: the effect of both these solutes has been examined.

2. EXPERIMENTAL

The samples were in the form of polycrystalline buttons about 20 mm dia. and weighing about 12 g. These were made by arc melting and were examined in the as-cast state, the necessary flat, strain-free surface being obtained by grinding and then electropolishing.

The uranium used had a total metallic impurity content of about 40 ppm of which about 25 ppm was silicon, while the plutonium contained about 300 ppm total impurities of which about 60 ppm was tungsten. The available neptunium was far less pure, —99.4 per cent—but it was only used in fairly dilute solution. The specimens were analysed for plutonium but the maximum deviation from the 'weighed out' compositions was found to be negligible—less than 1 per cent of the plutonium content.

The samples were examined using copper $K\alpha$ X-rays in a cryostat attached to a Hilger

and Watts diffractometer. Temperatures were measured by gold-cobalt vs. 'normal' silver thermocouples clamped to the opposite surface of the sample by a backing plate: temperatures are thought to be accurate to $\pm 1^\circ\text{K}$. Typically the angular positions of about 40 reflections between 50 and $145^\circ 2\theta$ were measured and a computer programme [21] based on Cohen's method [22] used to calculate the lattice parameters. Although the cryostat was centred to the diffractometer axis before each experiment there was usually a slight residual misalignment which was eliminated using the $\cos \theta \cot \theta$ extrapolation function. The probable errors in the lattice parameters as shown in the diagrams are derived from the scatter between the various reflections.

3. RESULTS AND DISCUSSION

(a) Pure uranium

The lattice parameters obtained for an unalloyed specimen are shown in Fig. 1 and the cell-volumes in Fig. 2.

Quantitatively the results agree with the work of Barrett *et al.* [3] but for each parameter the change is rather smaller, as is shown in Table 1.

The reason for the discrepancy is not clear but may be due to the effect of small amounts of impurities. The agreement between the present work and the dilatometric work of Hough *et al.* [4] is however good, although the samples were not from the same source.

Apart from the slight relative movements of some of the reflections caused by the anisotropic nature of the transformation no change in the X-ray pattern was observed at any temperature: the changes in intensity in

Table 1. Changes in lattice parameters and cell volume in α -uranium between 50 and 4.2°K

x	a	b	c	v
Present work	+0.0063 Å	+0.0019	−0.0034	0.154
Ref. [3]	+0.0080	+0.0023	−0.0047	0.185

Table 2. Comparison of relative volume changes in α -uranium between 50 and 4.2°K obtained by different techniques

	Present work	Ref.[3]	Ref.[4]
$\frac{\Delta V}{V}$	0.00188	0.00225	0.00189
	(X-rays)	(X-rays)	(dilatometer)

some reflections caused by the variation in the y parameter[3] were not significant in the polycrystal technique used. The observed reflections remained sharp at all temperatures and there was no suggestion of line splitting. This would have been observed if a two phase ($\alpha + \alpha_0$) region had existed between 20–35°K as proposed by

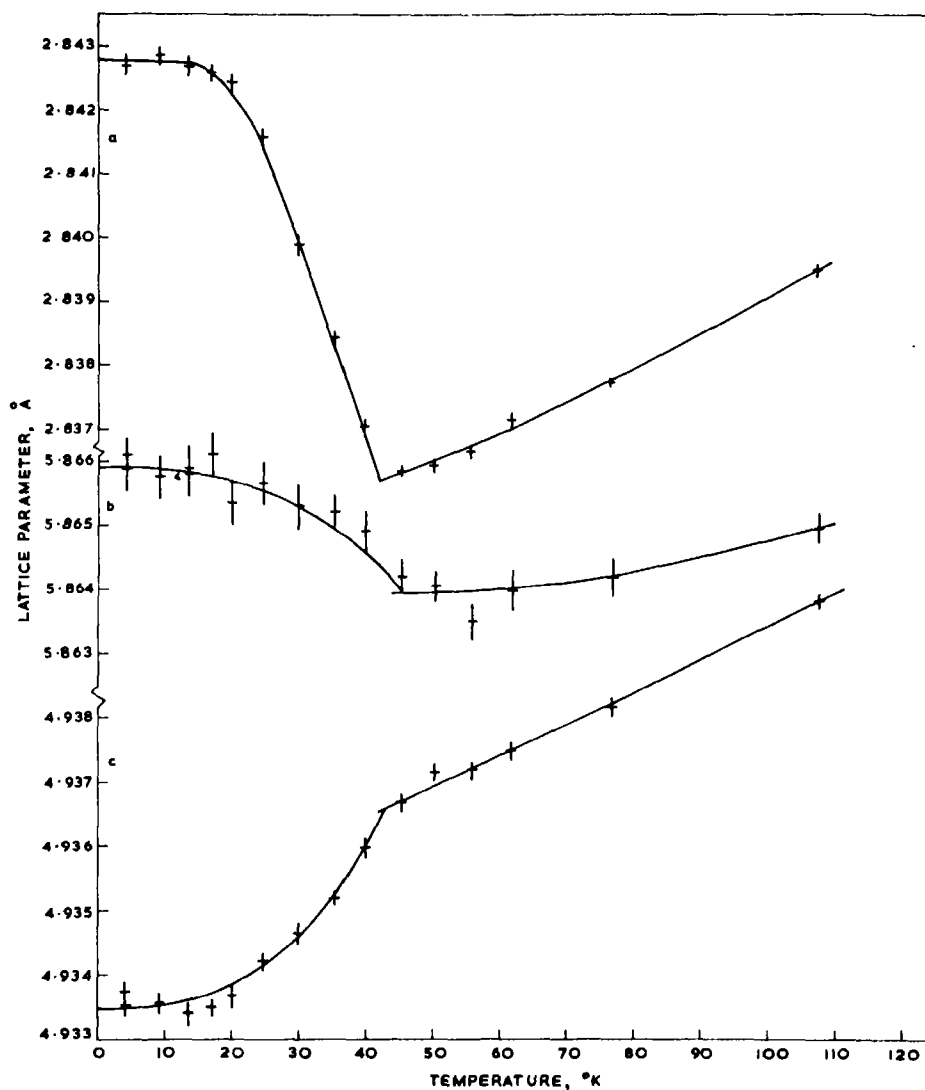


Fig. 1. Variation of lattice parameters with temperature for α -uranium.

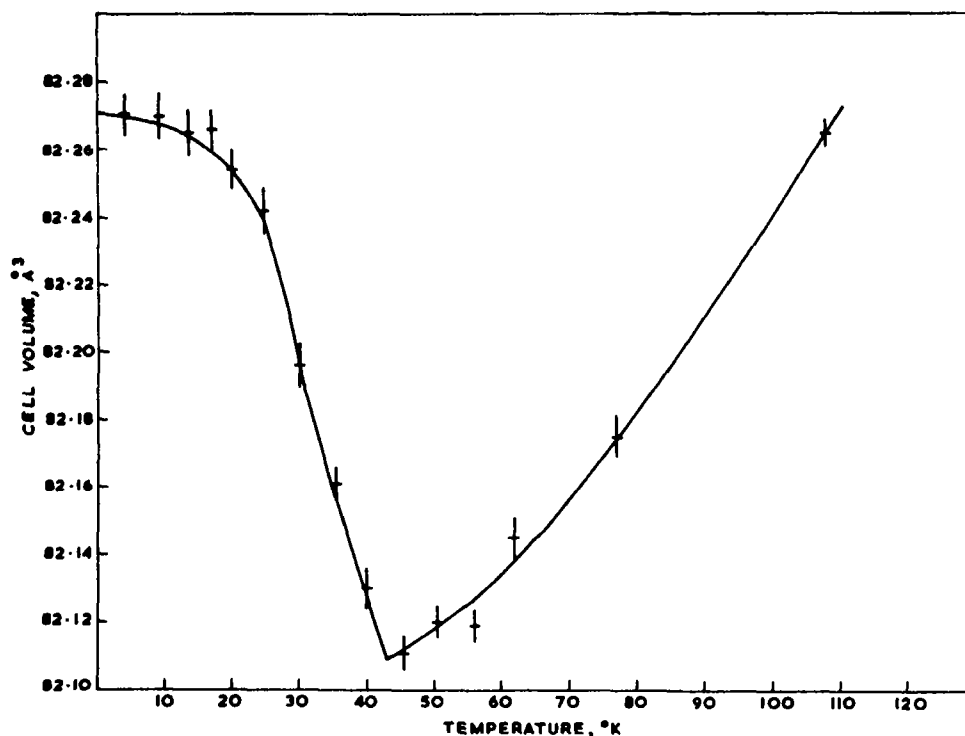


Fig. 2 The effect of temperature on the cell volume of α -uranium.

Fisher and Dever[8] to account for their elastic moduli results (α_0 denotes the low temperature modification of α). Such line splitting would have been readily observed since the changes in line position on transforming from α at 43°K to α_0 at 4°K are quite large, e.g. for (213) the change in 2θ is 0.4°—about the same as the separation between the $K\alpha_1$ and $K\alpha_2$ reflections at that angle ($\sim 124^\circ$).

An approximation to the energy involved in the transition may be obtained from the total volume change. If the 5.5 at% plutonium alloy (see below) is assumed to demonstrate normal behaviour then the volume change (ΔV) in transforming from α to α_0 at 4°K may be calculated. The energy difference is:

$$E = \frac{(\Delta V)^2}{2\chi V}$$

where V = the cell volume (82.0Å^3)
 χ = the volume compressibility
 $(1.2 \times 10^{-12} \text{ cm}^2/\text{dyn})$
 $\Delta V = 0.23\text{Å}^3$
 whence $\Delta E = 4.0 \text{ J/g.atom.}$

This compares with $\Delta E = 7.8 \text{ J/g.atom}$ determined from the excess specific heat in the 43°K region[13]. The difference between these two figures is not surprising in view of the approximate nature of the calculation and the large—and to some extent uncertain—variation of the compressibility with temperature.

Comparison of the V vs. T curves for pure α -Uranium and for U 5.5 at% Pu also shows that α -Uranium deviates from 'normal' expansion behaviour well above 43°K. This also occurs in some other properties, notably the specific heat [13].

(b) *Uranium plutonium alloys*

Plutonium in solution has two effects on the anomaly. These are shown in Figs. 3 and 4 where the cell volume and the 'a' parameter are plotted against temperature for the various alloys used. In these figures the results for all the alloys have been 'normalised' at 77°K to the 5.5 at% Pu curve to eliminate the effects of composition at this temperature and to remove small systematic variations between the various runs. The effect of plutonium additions on the other parameters was similar but not so clear cut as the parameter changes were smaller.

As the concentration of plutonium was increased the temperature at which the minimum occurred was progressively reduced. The temperatures obtained from both V vs. T and 'a' vs. T curves are plotted against composition in Fig. 5. For the higher concentrations where the size of the anomaly is small there is considerable uncertainty in the temperature because it was difficult to decide where the two branches of the curves met.

The second and more obvious effect of plutonium is to reduce the size of the anomaly. This occurs in all three parameters and so the results are only shown for the cell volume and the a parameter where the experimental scatter is least. These are plotted against plutonium concentration in Fig. 6. To obtain these figures it was necessary to determine a reference line; this would be provided by an alloy in which the anomaly was completely absent and which behaved normally, with the expansion coefficient increasing steadily with temperature. The 5.5 at% plutonium alloy was selected for this since no unusual behaviour was found in any of the parameter vs. temperature plots. The results shown in Fig. 6 are therefore obtained by subtracting the cell volume or lattice parameter at 4.2°K for the 5.5 at% plutonium alloy from the normalised value at this temperature for the other alloys.

The observed behaviour is consistent with the electron transfer theory of Geballe *et al.*[15]. For transfer to the localised 5f band to occur it must be assumed that this band is reduced in energy as the temperature is lowered and that the lower energy edge of this band crosses the Fermi surface, near 43°K, where electron transfer starts; this band is further lowered in energy with further reduction in temperature from 43°K to about 20°K. Below 20°K, however, as shown in Fig. 2. and in Refs.[1], [3] and [4], little further increase in volume occurs and it can be assumed that the occupancy of the 5f band does not change significantly below this temperature.

On the Zachariasen scheme of valencies [23], plutonium has 3 non-bonding 5f electrons, and only 5 valency electrons compared with 6 for uranium. With the size factor small, only about 3 per cent, it is assumed that to a first approximation the effect of plutonium in solution is to lower the Fermi level, the band structure remaining unaffected. In the alloys therefore the uranium f -band lies further above the Fermi level and a lower temperature must be reached before it is sufficiently lowered in energy to touch the Fermi surface: i.e. the temperature at which the anomaly occurs is reduced. Further, the overlap with the Fermi surface at 4°K will be less in the alloys and fewer electrons will be transferred; thus the size of the anomaly will also be reduced. Adding 4 at% plutonium reduces the electron to atom ratio by 0.04 and this (Fig. 6) is sufficient to suppress the anomaly completely in quantitative agreement with the Geballe hypothesis. This addition is sufficient to reduce the temperature at which the transition starts to about 20°K in agreement with the suggestion that little change in the occupancy of the 5f band occurs below this temperature.

(c) *Uranium-neptunium alloys*

The results for these alloys are difficult

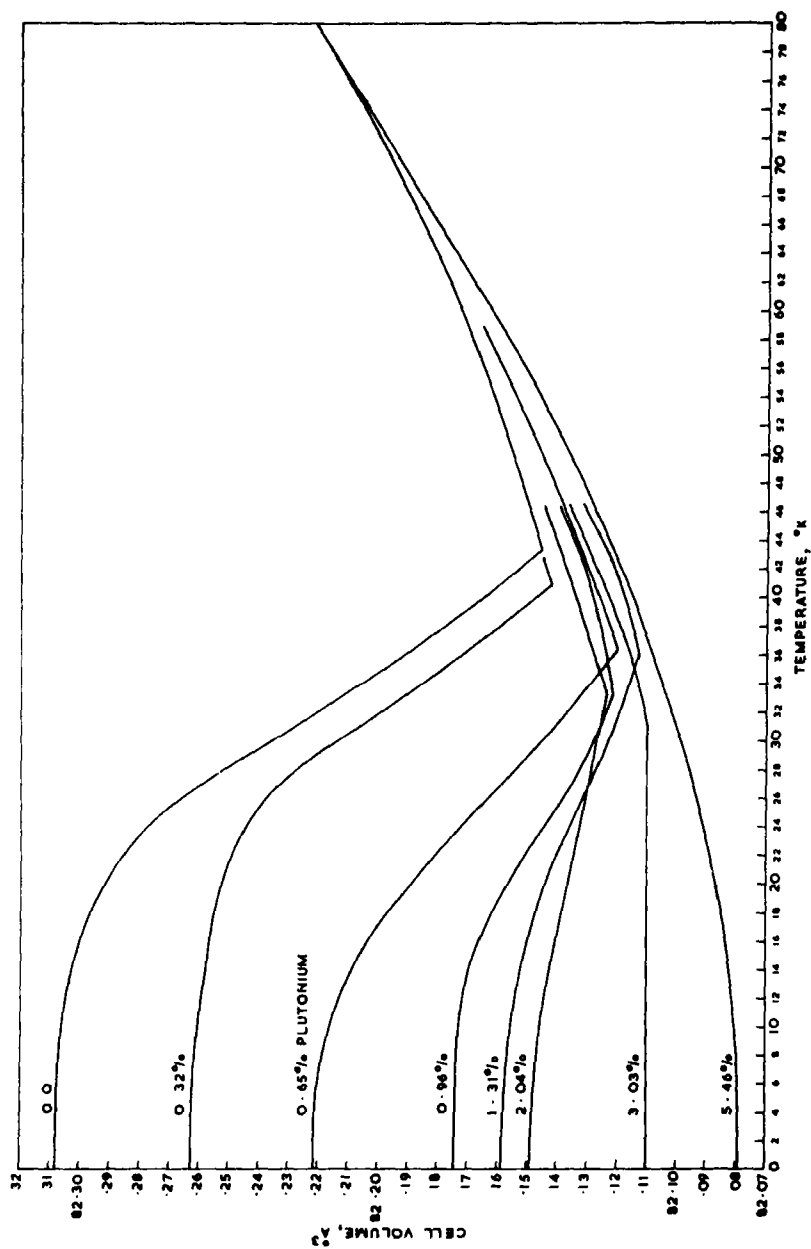


Fig. 3. The variation of cell volume with temperature in some uranium-plutonium alloys (normalized at 77°K).

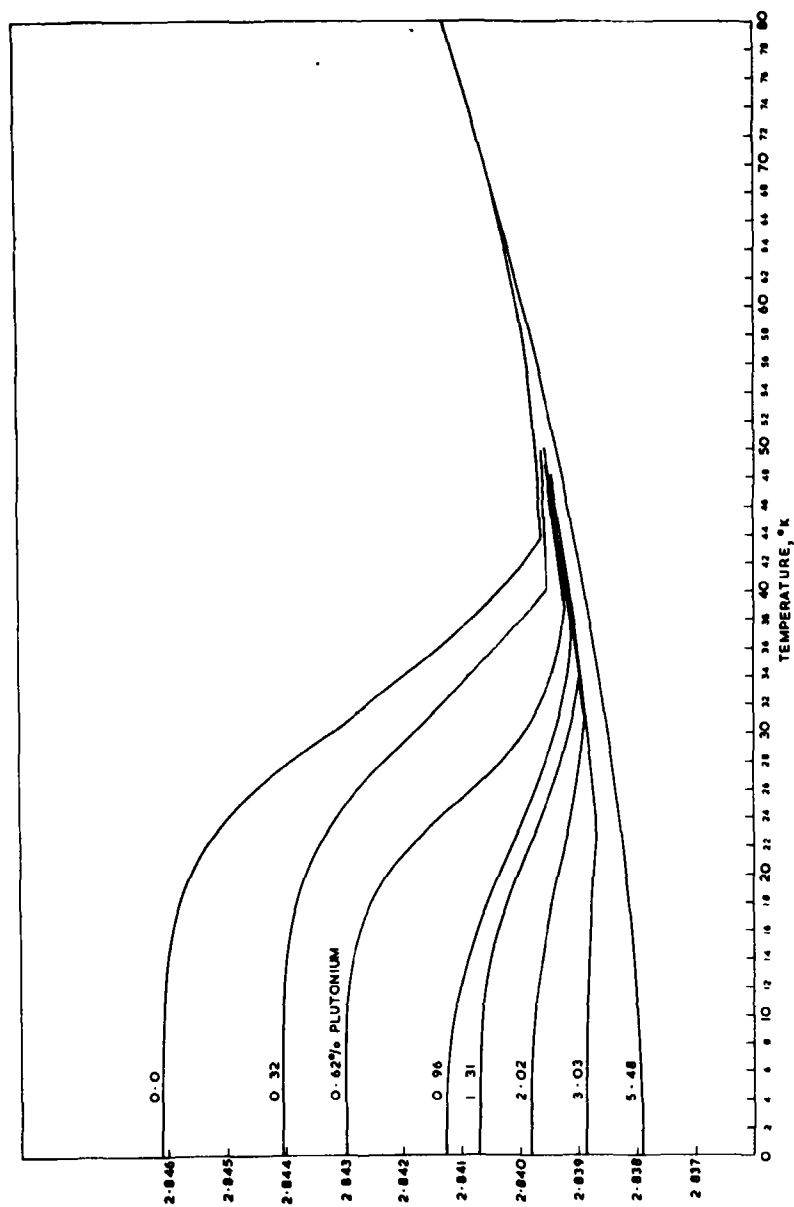


Fig. 4. The variation of the 'α' parameter with temperature in some uranium-plutonium alloys (normalized at 77°K).

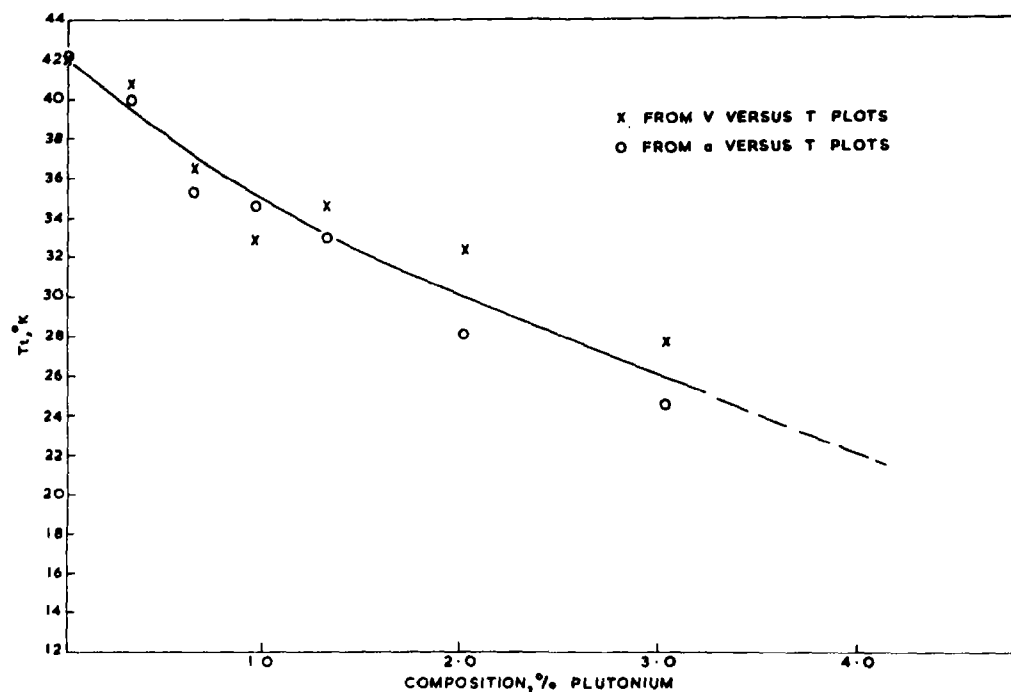


Fig. 5. The transition temperature of some uranium-plutonium alloys.

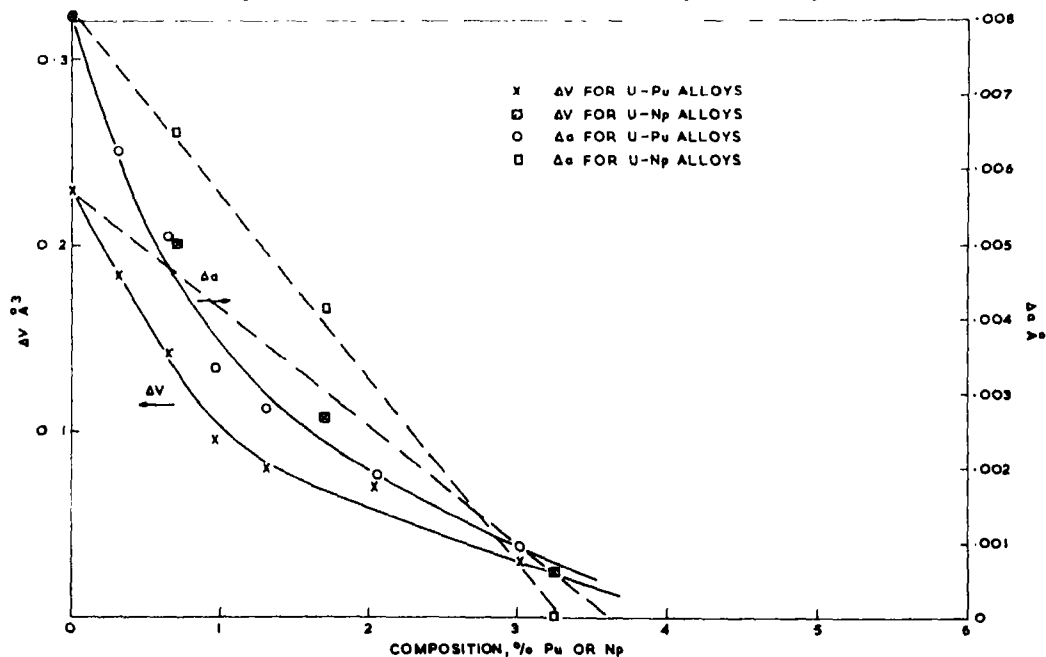


Fig. 6. The magnitude of the anomaly in uranium-plutonium and uranium-neptunium alloys.

to interpret because at the lowest temperatures they become 'two phase'. On cooling, the cell volume and lattice parameters behaved in a manner similar to those for pure uranium metal or for the plutonium alloys until a few degrees below the α/α_0 transition temperature. Then some of the X-ray reflections split into two components, both however remaining reasonably sharp. The extra lines could be indexed on a second orthorhombic cell (α_0') with parameters slightly different from the main one, giving a rather larger cell volume. The intensities of the α_0' lines did not vary systematically either for any one alloy at a given temperature or with composition.

The normal α_0 parameters behaved like those of α_0 in the U-Pu alloys. The size of the dilation anomaly decreased with composition to zero at about 3.5 at% neptunium (Fig. 6). Similarly the temperature of the α/α_0 transition decreased with alloy content although rather irregularly due to experimental uncertainty.

The α_0' parameters for the 0.7 at% neptunium gave a cell volume at 4°K rather larger than that for pure α_0 uranium but this was reduced at higher neptunium concentrations. The significant difference between α_0 and α_0' occurs in the 'a' parameter.

The lattice parameters at 4°K of both α_0 and α_0' for the neptunium alloys are given in Table 3.

The possibility that the line splitting is attributable to specimen inhomogeneity

is ruled out by the sharpness of the X-ray reflections and the fact that this effect was never observed in U-Pu alloys produced in the same way. Nor could it be accounted for by a transition to a monoclinic structure as occurs for instance in some U-Nb alloys at room temperature (24): some of the line splitting (e.g. that of (200)) was incompatible with this suggestion.

The most likely explanation for this behaviour is that it is due to a shear transformation occurring in only some of the grains of the cast specimen and brought about by the strain produced by the anisotropic α/α_0 transition. Why such a shear transformation should occur in the neptunium but not in the plutonium alloys is not clear. Neptunium with a size factor near zero, a valency of 6 and only one f electron is more similar to uranium than is plutonium. It could be that chemical purity is an important factor since the neptunium used contained considerably more impurities than either the uranium or the plutonium.

(d) Possible effect on the superconducting transition

As noted above, it has been postulated [15-17] that α_0 uranium is not a superconductor, its apparent superconductivity being due to filaments of α , stabilised at the lowest temperatures by pressure. Under a pressure of 10 kbar the α/α_0 transition is suppressed and α is found to be a bulk superconductor with a T_c of about 2°K.

Table 3. Parameters of U-Np Alloys at 4°K

	U	UO 0.73 at% Np	U 1.74 at% Np	U 3.25 at% Np
α_0 a	2.8427 ± .0001	2.8410 ± .0001	2.8380 ± .0001	2.8329 ± .0001
b	5.8659 ± .0004	5.8635 ± .0005	5.8609 ± .0005	5.8604 ± .0004
c	4.9337 ± .0002	4.9354 ± .0004	4.9353 ± .0003	4.9347 ± .0004
V	82.270 ± .007	82.22 ± .02	82.09 ± .01	82.09 ± .008
α_0' a		2.8511 ± .0004	2.8482 ± .0005	2.8451 ± .0002
b		5.878 ± .010	5.868 ± .002	5.866 ± .001
c		4.918 ± .005	4.923 ± .003	4.926 ± .001
V		82.43 ± .16	82.28 ± .06	82.22 ± .03

In addition, α -phase U-Mo alloys, containing more than 5 at% Mo, were found to be bulk superconductors below 0.8°K [25]. Alloying with 4 at% plutonium also stabilizes the α -phase and on this count one would expect alloys containing more than this concentration to be bulk superconductors with a T_c approaching 2°K, though small concentrations of solutes often seem to reduce T_c and the localised 5f electrons associated with the plutonium atoms may also have this effect.

This series of alloys thus offers the possibility of establishing unambiguously whether or not the occurrence of superconductivity is associated directly with the α -phase. Experiments are in hand to resolve this question.

(e) *Relation with anomalies in other properties*

The electron transfer hypothesis adequately describes the changes in lattice parameters with temperature and with alloying additions and also the effect of pressure on the superconducting critical temperature. However, the magnetic susceptibility results suggest that the number of f electrons per atom cannot be as high as 0.04, if the moments are randomly oriented [12] and the small specific heat peak is suggestive of a co-operative phenomenon [13]. Further the elastic moduli vs. temperature curves for polycrystalline uranium [26] are of basically similar shape to those found for α -manganese [27] and for praseodymium and samarium [28] where the transitions are known to be magnetic in origin. It seems most probable then that the electron transfer to the 5f band is accompanied by some type of spin alignment [29]. It is possible that the reduction in energy of this band, necessary for the electron transfer, is caused by its division into magnetic sub-bands and that it is one of these which is populated below 43°K.

Acknowledgement—The author gratefully acknowledges the encouragement of many stimulating discussions with Dr. J. A. Lee.

REFERENCES

1. LAQUER H. L., *U.S. Atomic Energy Commission Rep. No. A.E.C.D. 3706* (1952).
2. BRIDGE J. P., SCHWARTZ C. M. and VAUGHN D. A., *Trans. AIME* **206**, 1282 (1956).
3. BARRETT C. S., MUELLER M. H. and HITTERMAN R. L., *Phys. Rev.* **129**, 625 (1963).
4. HOUGH A., MARPLES J. A. C., MORTIMER M. J. and LEE J. A., *Phys. Lett.* **27A**, 222 (1968).
5. ANDRES K., *Phys. Rev.* **170**, 614 (1968).
6. BERLINCOURT T. G., *Phys. Rev.* **114**, 969 (1959).
7. FISHER E. S. and McSKIMIN H. J., *Phys. Rev.* **124**, 67 (1961).
8. FISHER E. S. and DEVER D., *Phys. Rev.* **170**, 607 (1968).
9. MEADEN G. T., Thesis. University of Oxford (1962).
10. ARAJS S. and COLVIN R. V., *J. less-common Metals* **7**, 54 (1964).
11. JOUSSET J. C., *Acta metall.* **14**, 193 (1966).
12. ROSS J. W. and LAM D. J., *Phys. Rev.* **165**, 617 (1968).
13. LEE J. A., SUTCLIFFE P. W. and MENDELSSOHN K., *Phys. Lett.* **30A**, 106 (1969).
14. HALL R. O. A., To be published.
15. GEBALLE T. H., MATTHIAS B. T., ANDRES K., FISHER E. S., SMITH T. F. and ZACHARIASEN W. H., *Science* **152**, 755 (1966).
16. SMITH T. F. and GARDNER W. E., *Phys. Rev.* **140**, 1620 (1965).
17. HO J. C., PHILLIPS N. E. and SMITH T. F., *Phys. Rev. Lett.* **17**, 694 (1966).
18. ELLINGER F. H., ELLIOTT R. O. and CRAMER E. M., *J. nucl. Mater.* **1**, 233 (1959).
19. MARDON P. G. and PEARCE J. H., *J. less-common Metals* **1**, 467 (1959).
20. ROUGH F. A. and BAUER A. A., *Battelle Memorial Institute Rep. No. BMI 1300* (1958).
21. MARPLES J. A. C. and SHAW J. L., *U.K.A.E.A. Rep. No. AERE R 5210* (1966).
22. COHEN M. V., *Rev. scient. Instrum.* **6**, 68 (1935) and **7**, 155 (1936).
23. ZACHARIASEN W. H. and ELLINGER F. H., *J. chem. Phys.* **27**, 811 (1957).
24. TANGRI K. and CHAUDHURI D. K., *J. nucl. Mater.* **15**, 278 (1965).
25. GORDON J. E., GARDNER W. E., SMITH T. F., CHU C. W. and MAPLE M. B., *Phys. Rev.* **176**, 556 (1968).
26. ROSEN M., *Phys. Lett.* **28A**, 438 (1968).
27. ROSEN M., *Phys. Rev.* **165**, 357 (1968).
28. ROSEN M., *Phys. Rev.* **180**, 540 (1969).
29. GARDNER W. E. and SMITH T. F., *Phys. Rev.* **154**, 309 (1967).

AN X-RAY STUDY OF THE STRUCTURES OF UN, UP, US AND USe AT CRYOGENIC TEMPERATURES

J. A. C. MARPLES

Atomic Energy Research Establishment, Harwell, Berkshire, England

(Received 29 December 1969)

Abstract—The structures and lattice parameters of the compounds UN, UP, US and USe have been determined between 4°K and 300°K. UN has a negative expansion coefficient below the Néel temperature (52°K) and UP, while showing no change at its Néel temperature (122°K), exhibits a small expansion anomaly at 22°K. US and USe both become rhombohedral below their Curie temperatures (178 and 160°K). The lattice distortion may be correlated with published magnetisation results.

1. INTRODUCTION

AT ROOM temperature the mononitride, phosphide, sulphide and selenide of uranium all have the *B1*, face-centred cubic rock-salt structure. UN and UP are known to be anti-ferromagnetic with Néel temperatures (T_N) of about 52 and 122°K respectively. The variation of the specific heat of UN with temperature has been studied by Counsell *et al.*[1] and by Westrum and Barber[2] who found a small peak at T_N . The magnetic susceptibility has been investigated by Anderson and Dell[3] and the thermo-electric power and resistivity by Costa *et al.*[4]. Curry[5] determined the magnetic structure by neutron diffraction and showed that the ordering was of type 1 with the moments of the uranium atoms arranged in opposed ferromagnetic sheets.

The specific heat of UP has been determined by Counsell *et al.*[6] and the magnetic susceptibility by Albutt *et al.*[7]. The specific heat has a peak at the Néel temperature and an extra, very sharp peak at 22.5°K. Curry[8], in addition to showing that the magnetic structure was the same as for UN, also found that the intensity of the magnetic reflections increased markedly below this temperature (22.5°K). Further, magnetic susceptibility

measurements by Gardner[9] showed an abrupt decrease in the susceptibility below 20°K. This change was tentatively ascribed to an 'unidentified change in the electronic ground state'[6].

US is ferromagnetic with a Curie temperature of 178°K. Westrum has studied the specific heat[10] and Kazmierowicz[11] the galvanomagnetic properties—magnetisation, magnetoresistance and Hall effect. Wedgewood[12] showed that below the Curie temperature the magnetic moments were aligned along the (111) direction and suggested that this caused the symmetry to change to rhombohedral. This was confirmed by Wilson[12] in a preliminary X-ray examination. The magnetisation was also studied by Chechernikov[13].

USe was likewise shown to be ferromagnetic by Trzebiatowski[14] with a Curie temperature of 160°K whilst Chechernikov studied the magnetisation[13] and Takahashi and Westrum the specific heat[16]. The easy axis of magnetisation has not been determined.

The present experiments were undertaken in order to establish the crystal structures below the magnetic ordering temperatures and to determine whether changes in expansion coefficients occurred.

2. EXPERIMENTAL

The various samples were, using $\text{CuK}\alpha$ radiation, X-rayed in a cryostat which fits onto a standard Hilger and Watts diffractometer. The samples, in powder form, are glued onto a 2 mm thick metal mounting plate with shellac which was chosen as a cement because it has no X-ray pattern in the 2θ range of interest. The sample and mount are screwed into a copper holder which is soldered to the lower end of a connecting tube on the bottom of the liquid helium (or nitrogen) container. Temperatures are measured by gold-cobalt versus 'normal' silver thermocouples whose junctions are trapped between the mounting plate and a second backing plate. Temperatures, other than 4.2°K (with liquid helium in the inner container) or 77°K (liquid nitrogen), were obtained by passing a current through a heater wound on the copper holder. This vapourises the liquid in the connecting tube which then provides a poor conduction path to the liquid in the main container. The specimen temperature can then be controlled to about $\pm 1^\circ\text{K}$ using a normal temperature controller, with the connections reversed, operated by one of the thermocouples.

Temperature measurement is thought to be accurate to $\pm 1^\circ\text{K}$ below 100°K and to $\pm 2^\circ\text{K}$ above this temperature. The specimen is surrounded by two radiation shields, an outer one at 77°K and an inner one at either 4.2 or 77°K depending on the refrigerant used. The X-rays reach the specimen through a nickel foil window—which also acts as a $\text{CuK}\beta$ filter—in the first of these and beryllium windows in the inner shield and also in the outer vacuum can.

The intensity of the reflected X-rays is measured by a proportional counter and an amplifier, pulse-height analyser, ratemeter and strip chart recorder system. The specimen was aligned to the diffractometer axis at each temperature but any residual error from this cause was eliminated by extrapolating against $\cos \theta \cot \theta$. For the cubic substances this was done by a least squares method using six or

eight lines. For US, in the rhombohedral phase, the pattern was indexed as hexagonal and the parameters calculated by a computer program [17] based on Cohen's method [18]. The resulting parameters were then converted to rhombohedral (cell side and inter-axial angle).

The UN and UP samples used were taken from batches prepared for specific heat measurements and details are given in Refs. [1] and [6]. Briefly, the UN contained 0.14 wt. % O, presumably in solid solution as no UO_2 X-ray reflections were observed and the oxygen solubility is thought to be higher than this [1, 2, 19]. The UP contained 0.21 wt. % O, probably not in solution since a faint UO_2 (111) reflection was observed and the oxygen solubility is very low [20]. The UN contained ~ 400 ppm metallic impurities, the UP ~ 30 ppm.

The US was part of a batch obtained from Le Centre d'étude de l'énergie nucléaire, Mol, Belgium. Analysis showed that the oxygen content was less than 0.1 wt. %. The sulphur content was 11.7 ± 0.2 wt. %: the stoichiometric value is 11.85 wt. %. No second phase was detected by X-rays.

Use was made by reacting high purity U (~ 40 ppm total impurities) with Se (~ 5 ppm) in a glass tube at 700°C, pressing the powdered selenide formed into a pellet which was then argon arc melted. The resulting bead was crushed and some unreacted uranium removed—it did not of course crush. The Use was then made into the X-ray specimen in the way described above. This material was less satisfactory than the other three because it was not as well crystallised and gave a slightly 'blurred' X-ray pattern: the α_1 and α_2 reflections were resolved however at the higher angles.

3. RESULTS

(a) Uranium nitride

The lattice parameter vs. temperature curve is shown in Fig. 1. The error bars shown represent the probable error derived from the

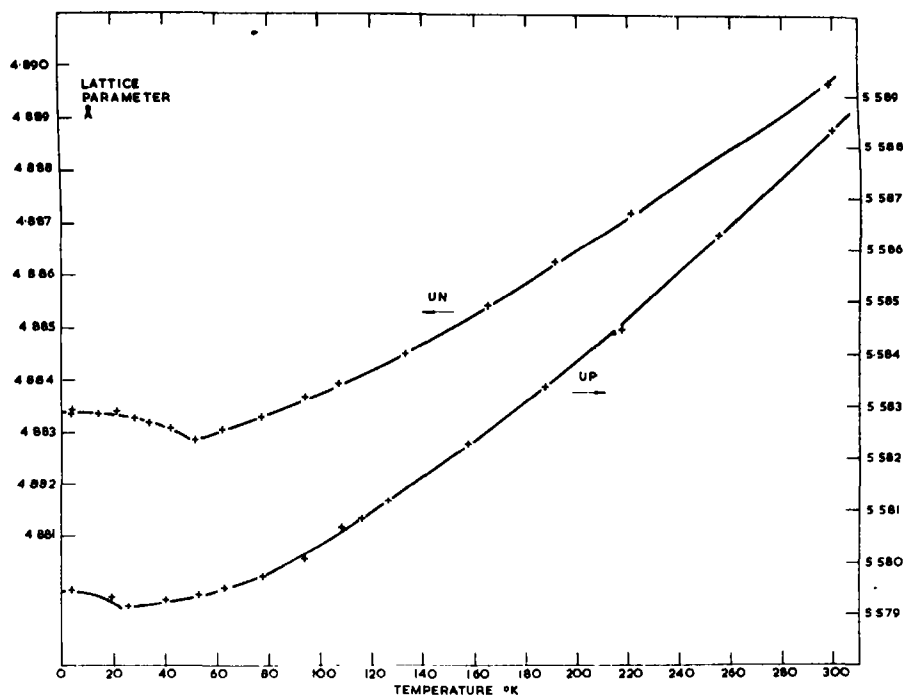


Fig. 1. Variation of lattice parameter with temperature for UN and UP.

'least squares' extrapolation. Whilst these are thought to be valid during the course of a run, the absolute error is probably rather larger. The most notable feature of the results is the change to a negative expansion coefficient below 51°K. The agreement is good between this temperature and the Néel temperature (52°K) determined from specific heat measurements[1].

(b) Uranium phosphide

The lattice parameter vs. temperature plot is also shown in Fig. 1. In contrast to UN there is no significant change in the expansion coefficient at the Néel temperature but at about 22°K there is either a step change in the lattice parameter or a change in expansion coefficient, again to a negative value. The effect is in any case quite small, about 1 part in 20,000; not much larger than the probable error in the results.

(c) Uranium sulphide

Below the Curie temperature, 178°K, the moments on the uranium atoms are aligned along the (111) direction, causing the structure to change to rhombohedral. The change in rhombohedral angle is plotted against temperature in Fig. 2. As the temperature is reduced below T_c , α decreases rapidly at first, though not apparently discontinuously, and then more gradually until at 4°K it reaches 89.6°. Over most of the range α was determined from measurements on about 20 lines as described above, but just below T_c it was felt to be more accurate to measure the separation of just one pair of well resolved lines—(420) and $(\bar{4}20)$ —and to use these to calculate α , since the small deviation from 90° produces a marked line splitting. The behaviour of line (420) over a range of 6°K is shown in Fig. 3: at 174°K the value of α is 89.88°. US also shows a change in expan-

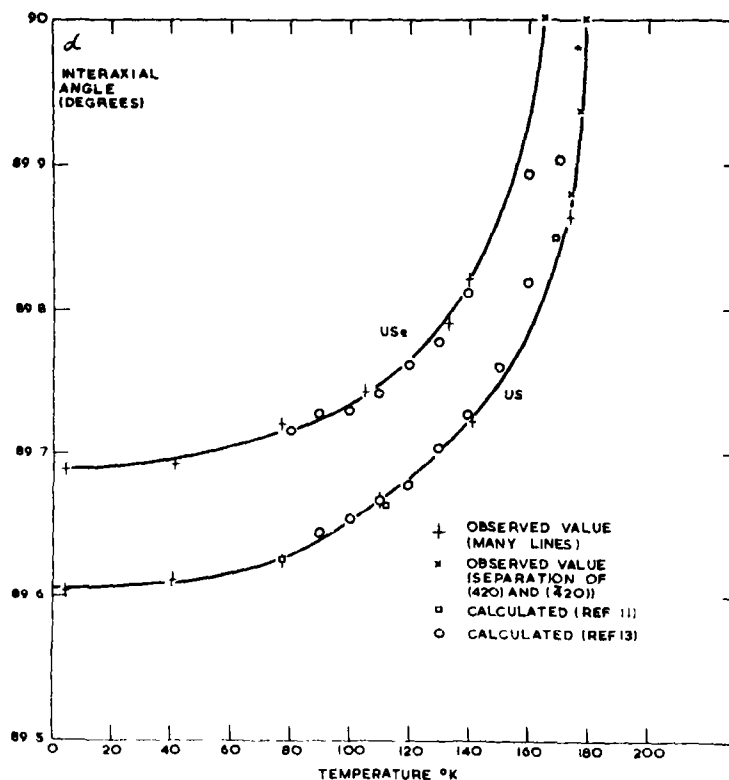


Fig. 2. Variation of interaxial angle with temperature for US and USe.

sion coefficient at the Curie temperature. This is shown in Fig. 4 where cell volume is plotted against temperature: cell volume is used rather than lattice parameter to allow for the change in inter-axial angle. Above T_c the linear expansion coefficient is $10.5 \times 10^{-6}/^\circ\text{K}$; below, $2.1 \times 10^{-6}/^\circ\text{K}$.

(d) Uranium selenide

As noted above, the easy direction of magnetisation has not been determined but it is presumed to be the same as in US because USe also becomes rhombohedral below the Curie temperature. The change in inter-axial angle is shown in Fig. 2. The X-ray reflections were not as sharp as for the US specimen and the variation of α near T_c could not be determined due to the overlap

of the α_1 and α_2 components. Otherwise the behaviour is very similar to US except that the change in interaxial angle is smaller by about 20 per cent. The variation of cell volume with temperature is shown in Fig. 4. The 'step' at the Curie temperature of about 1 part in 1000 may be produced by the additional broadening of the lines when the inter-axial angle is only just below 90° .

4. DISCUSSION

The uranium atom has six electrons outside the radon core. In the metal, these are thought all to lie in a combined $6d\ 7s$ valency band, although the $5f$ band is probably only just above the Fermi surface: it has been suggested that transfer of electrons to this band is the explanation of the 43°K expansion

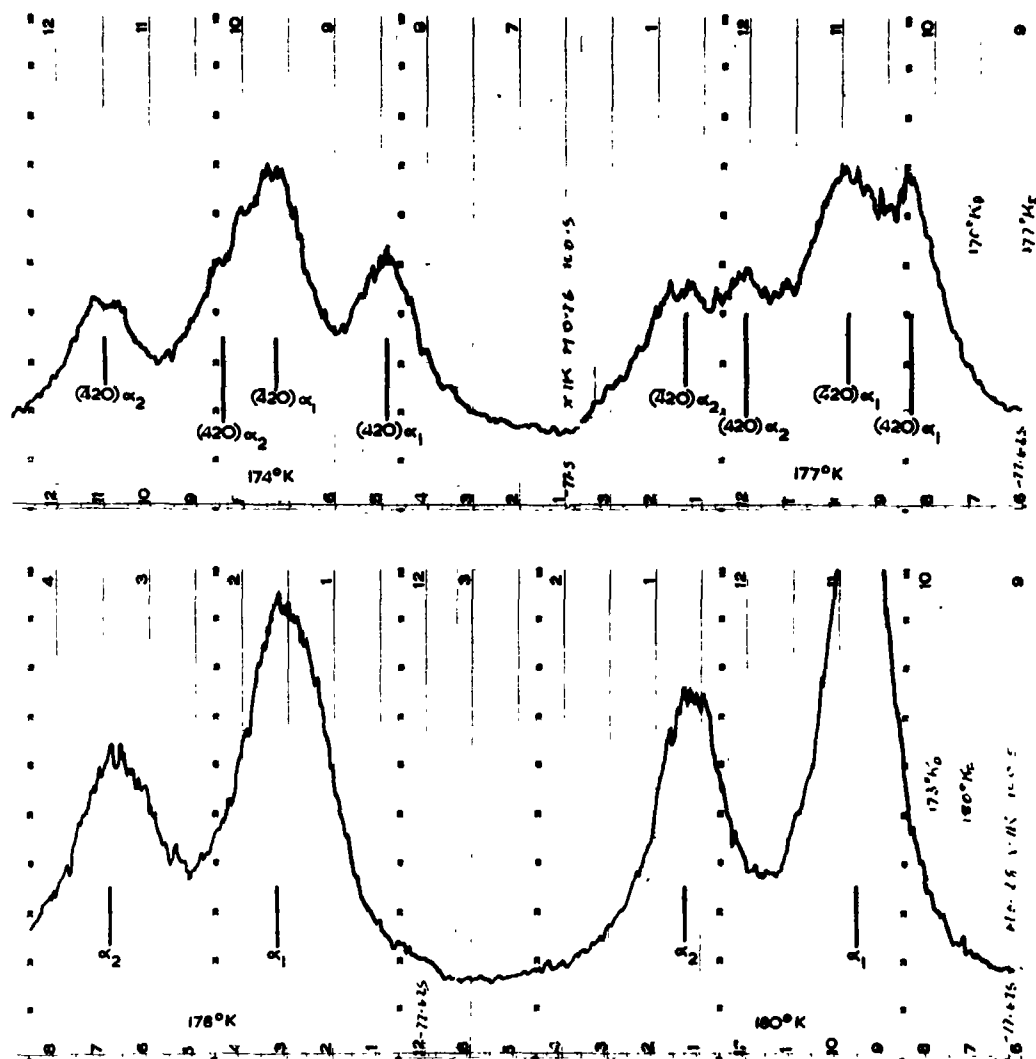


Fig. 3. Diffractometer traces illustrating the splitting of the (420) reflection at the cubic to rhombohedral transition in US at 179°K.

anomaly[21]. In the compounds, the 5f band is lowered in energy to overlap the Fermi surface and is partly occupied[7]: these 5f electrons are localised on the uranium atom and, since their spins are not compensated, are the source of the magnetic properties. It is against this background

that the results for the individual compounds will be discussed.

(a) Uranium nitride

Many antiferromagnetic materials have a negative magnetic Gruneisen parameter[22], leading in some cases to an overall negative

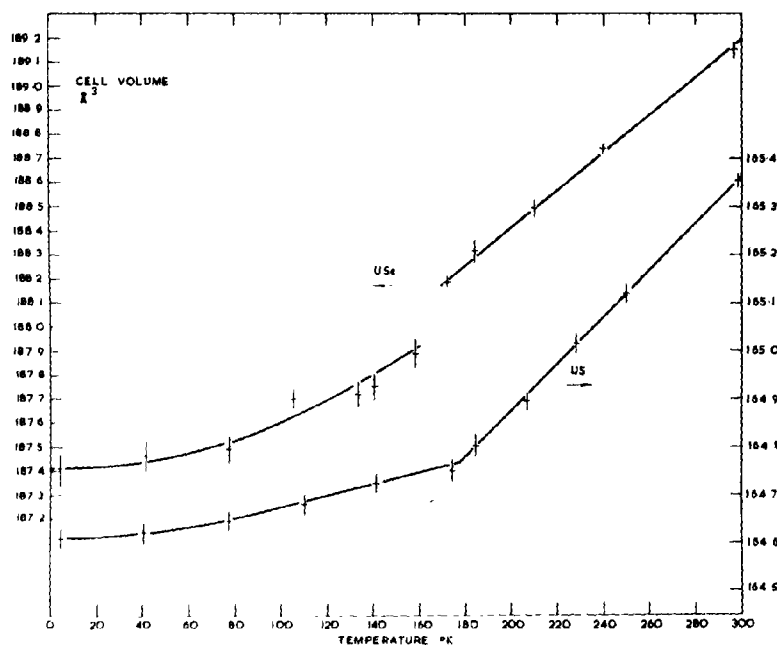


Fig. 4. Variation of cell volume with temperature for US and USe.

expansion coefficient, particularly at the lowest temperatures. A good example is α -manganese which has a negative expansion coefficient proportional to T below the Néel temperature (95°K) [22, 23]. In the present case the lattice parameters for UN below the Néel temperature, plotted against T^2 , also lie on a straight line (Fig. 5) showing that here too the expansion coefficient is proportional to T . The data can be represented by:

$$a = (4.88340 \pm 0.00002) - (2.05 \pm 0.15) \times 10^{-7} T^2 \text{ and } \alpha = -(8.4 \pm 0.6) \times 10^{-8} T.$$

(b) *Uranium phosphide*

In contrast to UN, UP shows no sudden change in expansion coefficient at the Néel point—less than $\pm 0.2 \times 10^{-6}/^\circ\text{K}$ in $6.0 \times 10^{-6}/^\circ\text{K}$ (Fig. 1). Both UN and UP have the same

magnetic structure whilst the magnetic moment and the entropy and enthalpy of the transition are all greater for UP (Table 1), [1, 6] and might be expected to indicate a greater not a lesser interaction in UP. The lattice parameter of UP is, however, rather larger than UN and consequently the U-U

Table 1. Data for UN and UP
(Refs. [1] and [6])

	UN	UP
Magnetic moment (Bohr magnetons)	0.75	1.7
Entropy of transition (cal. mole ⁻¹ deg ⁻¹)	0.15	0.74
Heat of transition (cal. mole ⁻¹)	7.1	87.3
Lattice parameter (Å)	4.89	5.59
U-U distance (Å)	3.46	3.95
γ (cal. deg ⁻² mole ⁻¹)	8.1×10^{-3}	2.3×10^{-3}
β (cal. deg ⁻⁴ mole ⁻¹)	4.4×10^{-5}	8.2×10^{-5}

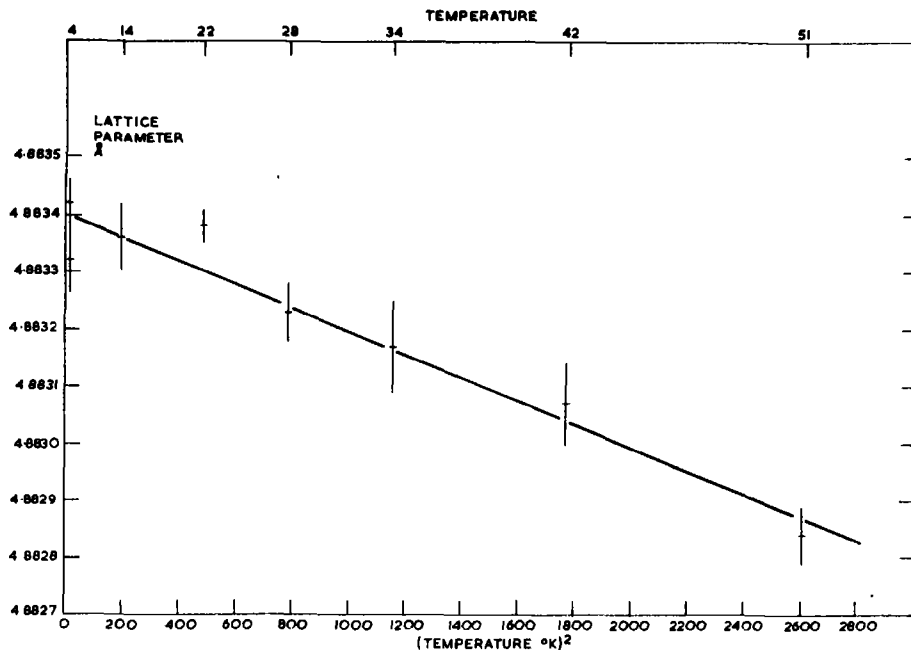


Fig. 5. The lattice parameter of UN plotted against the square of the absolute temperature.

separation is greater. Thus the overlap of the 5f electrons orbitals from neighbouring U atoms will be less for UP and the interaction between them correspondingly weaker.

UN and UP also differ in their low temperature specific heats. If the electronic and lattice terms are separated in the usual manner.

$$C_p = \gamma T + \beta T^3$$

it can be seen (Table 1) that the electronic contribution and hence also the density of states at the Fermi surface is about four times higher in UN than in UP. The most likely cause of this is that the Fermi surface lies near the peak of the narrow uranium 5f band in UN. If the antiferromagnetic ordering stabilises the 5f band with respect to the valency band then some transfer of electrons to the 5f band will occur, expanding the lattice both because of the enlargement of the

uranium atom (the 5f electrons are assumed to be localised) and because of the corresponding weakening of the bonding. Following Geballe *et al.*[21] and comparing the change in atomic radius derived from lattice parameter measurements with the atomic radii for 5- and 6-valent uranium it can be shown that the necessary electron transfer is only 0.009 electrons per atom. A redistribution of electrons among the available orbitals has previously been suggested[1] for UN as an explanation of the low entropy change observed at T_N and of the changes in electrical resistivity, magnetic moment and thermoelectric power.

With a lower density of states at the Fermi surface in UP, (the electronic specific heat is much smaller) the interband transfer would be expected to occur to a much lesser extent—or not at all—and no change in expansion coefficient is observed.

The cause of the small contraction on heat-

ing UP to 22°K is obscure. It coincides with a very sharp specific heat peak [6], about $\frac{1}{10}$ the size of that at T_N , whilst on heating through 22°K, the magnetic reflections in the neutron diffraction pattern were decreased in strength by 20 per cent [8]. The suggestion [6] that it corresponds to a change in the electronic ground state is quite plausible. If the number of conduction electrons was slightly reduced as a result, the decreased bonding would give an expansion.

(c) Uranium sulphide

Qualitatively, the rhombohedral distortion in US below the Curie temperature is obviously consistent with the magnetic structure determined by Wedgewood, the spins on the U atoms being aligned along the (111) direction. Becher and Döring [24] have shown by considering dipole-dipole interactions in a cubic lattice, that the longitudinal value of the magnetostriction, λ_{111} , is proportional to M_s^2 (the molecular field approximation also results in the anisotropy energy being proportional to M_s^2 [25]). Döring [26] showed that this proportionality is obeyed for nickel, although the relationship for iron is more complicated. For a small rhombohedral distortion to an interaxial angle $\alpha = 90 - \delta$, it can be shown by simple trigonometry that $\lambda_{111} = \delta$. Thus, if the U atoms can be treated, to a first approximation as interacting dipoles, $\delta \propto M_s^2$.

Kazmierowicz [11] determined the saturation magnetisation at four temperatures: 4, 77, 112 and 169°K. Using the first of these to normalise the others to the α vs. T curve, the three points shown in Fig. 2 are obtained. These are in good agreement with the experimental curve. Chechernikov [14] determined the magnetisation from 77°K upwards and this temperature was used to normalise the results. Further his results did not extend to high enough fields to cause saturation and were extrapolated to determine the saturation values. The derived points are in good agreement with the experimental curve below

150°K although above this there is some deviation. This satisfactory agreement suggests that it may be justified in this instance to treat the lattice of U atoms as interacting dipoles.

(d) Uranium selenide

A similar treatment of Chechernikov's magnetisation results [14] for USe again yielded reasonable agreement with the α vs. T curve (Fig. 2) although the scatter was rather greater than before.

The distortion observed in USe was about 20 per cent less than in the sulphide. The reason for this may well lie in the larger lattice parameter (5.740 Å as against 5.486 Å), that is in the greater separation of the 5f orbitals.

Acknowledgements—The author acknowledges the help of many useful discussions with Dr. R. M. Dell, who also supplied the UN and UP samples, with Dr. W. E. Gardner and particularly with Dr. J. A. Lee and thanks the latter and Dr. L. E. Russell for their encouragement and interest in this work.

REFERENCES

1. COUNSELL J. F., DELL R. M., MARTIN J. F., *Trans. Faraday Soc.*, **62**, 173 (1966).
2. WESTRUM E. F. and BARBER C. M., *J. chem. Phys.* **45**, 635 (1966).
3. ANDERSON R. A. and DELL R. M., Unpublished.
4. COSTA P., LALLEMENT R., ANSELIN F. and ROSSIGNOL D., *Compounds of interest in Nuclear Reactor Technology* (Edited by J. T. Waber, P. Chiotti, W. N. Miner.), p. 83. Am. Inst. Mining, Met. Petrol Engineers (1964).
5. CURRY N. A., *Proc. phys. Soc.* **86**, 1193 (1965).
6. COUNSELL J. F., DELL R. M., JUNKINSON A. R. and MARTIN J. F., *Trans. Faraday Soc.*, **63**, 72 (1967).
7. ALLBUTT M., JUNKINSON A. R. and DELL R. M., *Compounds of Interest in Nuclear Reactor Technology*. (Edited by J. T. Waber, P. Chiotti and W. N. Miner), p. 65. Am. Inst. Mining, Met. Petrol Engineers (1964).
8. CURRY N. A., *Proc. phys. Soc.* **89**, 427 (1966).
9. GARDNER W. E., Unpublished.
10. WESTRUM E. F., WALTERS R. R., FLOTOW H. E. and OSBOURNE D. W., *J. chem. Phys.*, **48**, 155 (1968).
11. KAZMIEROWICZ C. W., *Argonne National Lab. Rep. No. ANL-6731* (1963).
12. WEDGEWOOD A., private communication.
13. WILSON S. A., private communication.

14. CHECHERNIKOV V. I., *J. exp. theor. Phys.* **53**, 498 (1967).
15. TRZEBIATOWSKI W. and SUSKI W., Bull. de l'academie polonaise des sciences. *Chimie* **10**, 399 (1962).
16. TAKAHASHI Y. and WESTRUM E. F., *J. phys. Chem.* **69**, 3618 (1965).
17. MARPLES J. A. C. and SHAW J. L., *U.K.A.E.A. Rep. No. AERE-R 5210* (1966).
18. COHEN M. V., *Rev. scient. Instrum.* **6**, 68 (1935) and **7**, 155 (1936).
19. BLUMP L. et al., *Compte rend.* **C266**, 1456 (1968).
20. BASKIN Y., *J. Am. ceram. Soc.*, **48**, 652 (1965).
21. GEBALLE T. H. et al., *Science* **152**, 755 (1966).
22. WHITE G. K., *Proc. phys. Soc.* **86**, 159 (1965).
23. MARPLES J. A. C., *Phys. Lett.* **24A**, 207 (1967).
24. BECHER R. and DÖRING W., *Ferromagnetismus*. Springer, Berlin. Reprinted J. W. Edwards, Ann Arbor (1939).
25. KANAMORI K., *Magnetism I*. 171 (Edited by G. I. Rado and H. Suhl). Academic Press, New York (1963).
26. DÖRING W., *Z. Phys.* **103**, 560 (1936).

THERMODYNAMIC PROPERTIES OF SOLID Ar, Kr AND Xe BASED UPON A SHORT RANGE CENTRAL FORCE AND THE IMPROVED SELF-CONSISTENT PHONON SCHEME

M. L. KLEIN

Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada

and

V. V. GOLDMAN and G. K. HORTON

Department of Physics, Rutgers University, New Brunswick, N.J. 08903, U.S.A.

(Received 5 January 1970)

Abstract—The thermodynamic properties of solid Ar, Kr and Xe are investigated within the framework of the self-consistent phonon method. We have used a central two-body potential of the Mie-Lennard-Jones type. The lowest order self-consistent scheme, the so-called self-consistent phonon harmonic approximation (SC), is shown to be inadequate. The effect of including, in the Helmholtz free energy, the leading terms omitted by the sca is examined in detail and a comparison is also made with our earlier work based on the Born-von Kármán approximation. We find substantial differences between the results based on different approximations to the free energy.

1. INTRODUCTION

IN A RECENT paper[1] the conventional perturbation expansion of the partition function was used to examine the thermodynamic properties of an fcc lattice with nearest neighbor central two-body forces. Specific application was made to the ideal noble gas solids Ar, Kr and Xe. Above about one third of the melting temperature of these solids, anharmonic effects, as determined from the leading anharmonic terms, were found to be unrealistically large. The results were interpreted as a break-down of the familiar Born-von Kármán theory of lattice dynamics associated with large (≥ 6 per cent) r.m.s. amplitude vibration of the atoms comprising the lattice.

The pioneering work on the problem of large amplitude vibrations in solids was first presented by Born[2] and further developed by Hooton[3]. Their work was primarily concerned with solid He. It was not followed up largely because the required computing facilities have become available only recently.

Various formulations of different aspects of the theory have been presented by Choquard [4], Koehler[5], Plakida and Siklos[6], Boccara and Sarma[7], Horner[8] and others. The theory has come to be known as the method of self-consistent phonons. The most comprehensive development is to be found in the work of Choquard[4]. The lowest order scheme, called the self-consistent harmonic approximation (SC) has been applied to solid Ar and Ne by Gillis, Werthamer and Koehler [9]. In this order, odd derivatives of the interatomic potential do not appear in the free energy. Since these terms are known[1] to be important in all noble gas crystals, a meaningful description of their crystal dynamics must include such terms. This leads us to the implementation of Choquard's second order self consistent scheme. The application of this scheme to a realistic crystal model will require considerable computational sophistication and as yet has not been attempted. In this paper we will show that it is likely that a full second-order calculation will be needed to understand

the very high temperature properties of solid Ar, Kr and Xe.

In the meantime, we further explore the content of a theory [10] which only retains the leading terms of the type appearing in the full second order scheme (ISC). Our preliminary results [10] for Ne and Ar were encouraging and we have presented our detailed application to solid Ne and its two isotopes elsewhere [11]. Koehler [12] has studied the problem of phonon energies and lifetimes in Ne using a similar scheme (but his particular application has not yet been justified). We have independently obtained related results [13] for Ar. In this paper we present the detailed results of our investigation of ISC. The relevant theory is presented in Section 2 and interatomic potentials are discussed in Section 3. In Section 4 we present our explicit results for solid Ar, Kr and Xe based on an (*m*-6) Mie-Lennard-Jones central, two-body potential acting between nearest neighbors. Our results are compared with the available experimental data. We stress that our paper is primarily an investigation of the role of vibrational anharmonicity in an fcc lattice with short range central forces and not an attempt to obtain interatomic potentials from the solid state data.

2. IMPROVED SELF-CONSISTENT PHONON SCHEME (ISC)

We are concerned with an fcc Bravais lattice composed of *N* particles of mass *M*. Let the position of each particle associated with the lattice site *s* be denoted by **r_s**. In terms of the displacements **X_s** from the equilibrium positions **R_s** we can write for the position coordinates **r_s** = **R_s** + **X_s**. Thus we obtain for the Hamiltonian of the crystal

$$H = \sum_s p_s^2/2M + V(\{\mathbf{r}_s\}).$$

$V(\{\mathbf{r}_s\})$ is the crystal potential energy which, in our application to noble gas crystals, will be composed of central two-body interactions. Thus

$$V(\{\mathbf{r}_s\}) = \frac{1}{2} \sum'_{s_1 s_2} \phi(|\mathbf{r}_{s_1} - \mathbf{r}_{s_2}|)$$

where $\phi(\mathbf{r})$ is the two-body potential. We expand this potential in a Taylor series about the equilibrium sites **R_s** and separate the harmonic part V_h , which is bilinear in the displacements **X_s**, and treat the remainder as a perturbation.

$$V = H_0 + V', \quad V' = V - V_h,$$

and

$$H_0 = \sum_s \mathbf{p}_s^2/2M + V_h.$$

We calculate the Helmholtz free energy *F* from the expression

$$-\beta F = \ln \{ \text{tr } e^{-\beta H} \}$$

where $\beta = 1/k_B T$ and *T* is the temperature.

Let us define the harmonic ensemble average of an operator *A* by the expression

$$\langle A \rangle_0 = \{ \text{tr } e^{-\beta H_0} A \} / \{ \text{tr } e^{-\beta H_0} \}.$$

It is then easy to show that

$$-\beta(F - F_0) = \ln \left\langle T_D \exp \left(- \int_0^\beta V'(\beta_1) d\beta_1 \right) \right\rangle_0$$

where $V'(\beta)$ is our perturbation operator in the interaction representation, or $V'(\beta) = e^{\beta H_0} V' e^{-\beta H_0}$, T_D orders time, and $\exp(-\beta F_0) = \text{Tr } \exp(-\beta H_0)$. We can now expand the above expression into cumulants χ_k .

$$-\beta(F - F_0) = \sum_{k=1}^{\infty} \frac{(-1)^k \chi_k}{k!}.$$

The first three cumulants are given by

$$\chi_1 = \int_0^\beta \langle V'(\beta_1) \rangle_0 d\beta_1, \quad (1)$$

$$\begin{aligned} \chi_2 = & \int_0^\beta \int_0^\beta d\beta_1 d\beta_2 \langle T_D V'(\beta_1) V'(\beta_2) \rangle_0 \\ & - \left[\int_0^\beta \langle V'(\beta_1) \rangle_0 d\beta_1 \right]^2, \end{aligned} \quad (2)$$

$$\begin{aligned} \chi_3 = & \int_0^\beta \int_0^\beta \int_0^\beta d\beta_1 d\beta_2 d\beta_3 \langle T_D V'(\beta_1) V'(\beta_2) \\ & \times V'(\beta_3) \rangle_0 - 3 \int_0^\beta \int_0^\beta d\beta_1 d\beta_2 \times \\ & \times \langle T_D V'(\beta_1) V'(\beta_2) \rangle_0 \int_0^\beta d\beta_1 \langle V'(\beta_1) \rangle_0 \\ & + 2 \left[\int_0^\beta d\beta_1 \langle V'(\beta_1) \rangle_0 \right]^3 \end{aligned} \quad (3)$$

When the potential V is expanded in a Taylor series the averages in the cumulants reduce to time ordered averages of products of the

diagrams contained in each of the cumulants. His first order scheme retains χ_1 , (Fig. 1(a)), together with the infinite set of ring diagrams based on this vertex. The ring diagram series is represented in Fig. 2 and the contribution to the free energy is shown in Fig. 3(a). To second order, the remaining (or irreducible) part of χ_2 , which has not been included in the first order ring diagram summation, is retained together with its ring diagrams. Self-consistency is obtained by solving for the optimum harmonic basis which will make

$$\chi_1 \sim \text{diagram} - \text{diagram} \quad (a)$$

$$\chi_2 \sim \text{diagram} - \text{diagram} + \text{diagram} - \text{diagram} + \text{diagram} - \text{diagram} + \dots \quad (b)$$

Fig. 1. Diagrammatic representation of the terms contributing to the first (a) and second (b) cumulants in the expansion of the partition function.

displacements. From the theorem[4] of Bloch and de Dominicis we know that these averages can be expressed in terms of averages of time ordered pairs only. Using diagrammatic analysis one can show that of the uncorrelated averages we have just considered only linked diagrams contribute to each cumulant and, therefore, to F . We indicate this by the subscript L . Thus we obtain

$$\begin{aligned} \chi_1 = & \int_0^\beta d\beta_1 \langle V'(\beta_1) \rangle_0 = \int_0^\beta d\beta_1 \langle V(\beta_1) \\ & - V_h(\beta_1) \rangle_{0,L} \\ \chi_2 = & \int_0^\beta \int_0^\beta d\beta_1 d\beta_2 \langle T_D V'(\beta_1) V'(\beta_2) \rangle_{0,L} \\ = & \int_0^\beta \int_0^\beta d\beta_1 d\beta_2 \langle T_D \{ V(\beta_1) - V_h(\beta_1) \} \\ & \times \{ V(\beta_2) - V_h(\beta_2) \} \rangle_{0,L} \end{aligned}$$

and so on. The cumulants are shown diagrammatically in Fig. 1. Choquard has carried out a resummation to infinite order of selected

$$\text{diagram} + \text{diagram} + \text{diagram} + \text{diagram} + \dots$$

Fig. 2. Diagrammatic representation of the terms contributing to the partition function in the 1st order ring diagram summation.

$$\text{diagram} + \sum \text{RINGS} (\text{diagram}) \quad (a)$$

$$\text{diagram} + \text{diagram} + \text{diagram} + \sum \text{RINGS} (\text{diagram}, \text{diagram}, \dots, \text{diagram}) \quad (b)$$

$$\text{diagram} + \text{diagram} \quad (c)$$

Fig. 3. Schematic representation of the free energy expansion in 1st order (a) and 2nd order (b). (c) Examples of basic terms contributing to the expansion of the free energy in the 3rd order.

the contribution of the ring diagrams vanish in each order. We find that to first order, the frequencies $\omega_{\mathbf{q}}$ and the eigenvectors $\mathbf{e}_\alpha(\mathbf{q})$ are obtained by solving the following equations self-consistently:

$$\begin{aligned} D_{\alpha\beta}(\mathbf{q}) &= \frac{1}{M} \sum_{\mathbf{p}} [1 - \cos(\mathbf{q} \cdot \mathbf{R}_{\mathbf{p}})] \langle \phi_{\alpha\beta}(\mathbf{R}_{\mathbf{p}}) \rangle \\ \omega_{\mathbf{q}}^2 &= \mathbf{e}_\alpha(\mathbf{q}) D_{\alpha\beta}(\mathbf{q}) \mathbf{e}_\beta(\mathbf{q}) \\ \langle \phi_{\alpha\beta}(\mathbf{R}_{\mathbf{p}}) \rangle &= (8\pi^3 \det \lambda_{\mathbf{p}})^{-1/2} \\ &\quad \times \int d\tau \exp\left(-\frac{1}{2} \tau \cdot \lambda_{\mathbf{p}}^{-1} \cdot \tau\right) \\ &\quad \times \phi_{\alpha\beta}(\mathbf{R}_{\mathbf{p}} + \tau) \\ (\lambda_{\mathbf{p}})_{\alpha\beta} &= \frac{2}{MN} \sum_{\mathbf{q}} [1 - \cos(\mathbf{q} \cdot \mathbf{R}_{\mathbf{p}})] \frac{\mu_{\mathbf{q}\ell}}{\omega_{\mathbf{q}}^2} \\ &\quad \times e_\alpha(\mathbf{q}) e_\beta(\mathbf{q}). \end{aligned}$$

The resultant free energy is given by

$$\begin{aligned} F_{\text{sc}} &= \frac{N}{2} \sum_{\mathbf{p}} \langle \phi(\mathbf{R}_{\mathbf{p}}) \rangle + \sum_{\mathbf{q}} \\ &\quad \times \left\{ \beta^{-1} \ln \left[2 \sinh \left(\frac{\hbar \beta \omega_{\mathbf{q}}}{2} \right) \right] \right. \\ &\quad \times \left. \frac{\hbar \omega_{\mathbf{q}}}{4} \coth \left(\frac{\hbar \beta \omega_{\mathbf{q}}}{2} \right) \right\} \end{aligned}$$

where $\mu_{\mathbf{q}} = \hbar \omega_{\mathbf{q}} (n_{\mathbf{q}} + \frac{1}{2})$ and $n_{\mathbf{q}} = (\exp(\beta \hbar \omega_{\mathbf{q}}) - 1)^{-1}$ and ϕ_α , $\phi_{\alpha\beta}$, etc. are the tensor gradients of the two-body potential $\phi(r)$. In this order of approximation the entropy S_{sc} is that for a non-interacting system of Bose particles with energy $\hbar \omega_{\mathbf{q}}$ and pressure

$$P_{\text{sc}} = -(3v)^{-1} (N/2) \sum_{\mathbf{p}} \mathbf{R}_{\mathbf{p}} \cdot \nabla \phi(\mathbf{R}_{\mathbf{p}}).$$

To this order odd derivatives do not occur explicitly in the theory. Choquard has derived self-consistent schemes in which odd derivatives occur explicitly in the free energy. However, each order has a new set of self-consistent equations with new renormalized frequencies.

leading correction to F_{sc} coming from the irreducible part of χ_2 . This term can be shown to be

$$\begin{aligned} -\frac{N}{8} \sum_{\mathbf{p}, \mathbf{p}_1} \sum_{\sigma} \int_0^{\beta} d\tau \left\{ \left[\exp \lambda_{\mathbf{p}, \mathbf{p}_1}^{\sigma}(\tau) : \nabla_1 \nabla_2 - 1 \right. \right. \\ \left. \left. + \frac{1}{2} (\lambda_{\mathbf{p}, \mathbf{p}_1}^{\sigma}(\tau) : \nabla_1 \nabla_2)^2 \right] \exp \left(\frac{1}{2} \lambda_{\mathbf{p}_1} : \nabla_1 \nabla_1 \right) \right. \\ \left. \times \phi(\mathbf{R}_{\mathbf{p}_1}) \exp \left(\frac{1}{2} \lambda_{\mathbf{p}_1} : \nabla_2 \nabla_2 \right) \phi(\mathbf{R}_{\mathbf{p}_1}) \right\} \end{aligned}$$

where $\mathbf{p}_i$, s_i are lattice site labels and $\sigma = s_1 - s_2$

$$\begin{aligned} [\lambda_{\mathbf{p}, \mathbf{p}_1}^{(s_1 - s_2)}(\tau)]_{\alpha\beta} &= \langle T_D (X_{\mathbf{p}, s_1}^{\alpha}(\tau) - X_{s_1}^{\alpha}(\tau)) \\ &\quad \times (X_{\mathbf{p}_2 + s_2}^{\beta}(0) - X_{s_2}^{\beta}(0)) \rangle_{\text{sc}} \\ &= \frac{1}{MN} \sum_{\mathbf{q}} \frac{\hbar}{2\omega_{\mathbf{q}}} [n_{\mathbf{q}} e^{\hbar \omega_{\mathbf{q}} \mathbf{q} \cdot \mathbf{j} / \tau} \\ &\quad + (n_{\mathbf{q}} + 1) e^{-\hbar \omega_{\mathbf{q}} \mathbf{q} \cdot \mathbf{j} / \tau}] \\ &\quad \times (e^{-\mathbf{q} \cdot \mathbf{R}_1} - 1)(e^{-\mathbf{q} \cdot \mathbf{R}_2} - 1) \\ &\quad \times e^{\mathbf{q} \cdot \mathbf{R}_1} e_{\alpha}(\mathbf{q}) e_{\beta}(\mathbf{q}). \end{aligned}$$

The $X_i^{\alpha}(\beta)$ are the cartesian components of the displacement operator in the interaction representation. These two equations are formally those of Choquard's 2nd order theory except that here the implicit frequencies are of the first order. We simplify the above expression further by expanding the exponential $\exp(\lambda_{\mathbf{p}, \mathbf{p}_1}^{\sigma} : \nabla_1 \nabla_2)$ and retaining only the 3-phonon contribution. Thus we obtain

$$\begin{aligned} \Delta F &= -\frac{N}{8} \frac{1}{3!} \sum_{\mathbf{p}_1} \sum_{\mathbf{p}_2} \sum_{\sigma} \int_0^{\beta} d\tau [\lambda_{\mathbf{p}, \mathbf{p}_1}^{\sigma}(\tau)]_{\alpha\beta} \\ &\quad \times [\lambda_{\mathbf{p}, \mathbf{p}_1}^{\sigma}(\tau)]_{\gamma\delta} [\lambda_{\mathbf{p}, \mathbf{p}_1}^{\sigma}(\tau)]_{\epsilon\eta} \langle \phi_{\alpha\gamma\epsilon}(\mathbf{R}_{\mathbf{p}_1}) \rangle_{\text{sc}} \\ &\quad \times \langle \phi_{\beta\delta\eta}(\mathbf{R}_{\mathbf{p}_1}) \rangle_{\text{sc}}. \end{aligned}$$

On substituting for the λ 's the time integration can be carried out and we find our working equations

$$F = F_{\text{sc}}^{(1)} + \Delta F$$

$$\Delta F = \frac{-\hbar^2}{3NM^3} \sum_{123} \frac{\Delta(\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{q}_3)}{\omega_1 \omega_2 \omega_3} |\psi_{123}|^2 W_{123}$$

and

$$W_{123} = \frac{n_1 n_2 + n_2 n_3 + n_3 n_1 + n_1 + n_2 + n_3 + 1}{\omega_1 + \omega_2 + \omega_3} + \frac{3(n_2 n_3 + n_3 n_1 - n_1 n_2 + n_3)}{\omega_1 + \omega_2 - \omega_3}$$

$$\psi_{123} = \sum_{\rho} e^{i(\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{q}_3) \cdot \mathbf{R}_{\rho}/2} S_{\alpha}(1) S_{\beta}(2) S_{\gamma}(3) \times \langle \phi_{\alpha\beta\gamma}(\mathbf{R}_{\rho}) \rangle_{SC}$$

$$S_{\alpha}(1) = \sin(\mathbf{q}_1 \cdot \mathbf{R}_{\rho}/2) e_{\alpha}(\mathbf{q}_1 j_1).$$

This free energy has had some success in describing the thermodynamics of solid Ne and its isotopes[11], [14]. In the latter case, however, we have a much less severe test because of the restricted temperature range of that solid ($T < \Theta/3$).

3. INTERATOMIC POTENTIALS

Much has been written[15] recently about the interatomic potential for the noble gases, particular emphasis being placed on the inadequacies[16] of the various Mie-Lennard-Jones type potentials. In the solid there is now ample evidence that many-body forces are present. The exact nature of the non-pairwise additivity is still controversial but for Ar there may be some evidence that the 'triple-dipole' force of Axilrod and Teller is dominant. The situation with Kr and Xe, where many-body forces are relatively stronger, is by no means clear; we must await a reliable calculation of the dielectric function.

In this paper we want primarily to focus attention on the problem of how one calculates thermodynamic properties of the solid given the interatomic potential. At the present time it is by no means obvious how such a task should be performed. Thus we have used a phenomenological nearest neighbor central potential with parameters that fit the 0°K volume and the latent heat of the crystals[16]:

$$\phi(R_{\rho}) = \epsilon[(R_0/R_{\rho})^{12} - 2(R_0/R_{\rho})^6].$$

We also have results for the 13th power in the repulsive term and for all neighbor forces. These are available on request from MLK. We realize fully the limitations of this potential but, for the purpose of this paper, this is of secondary importance. It has the advantage that numerical calculations are considerably simplified and we can establish the range of validity of our dynamical model reasonably easily. Once the latter is known calculations based upon more realistic interatomic potentials would seem more appropriate[15].

4. RESULTS AND COMPARISON WITH EXPERIMENT

The details of the numerical work were already described in an earlier paper[11] and will not be repeated here. Our results are given in Figs. 4-22, where they are compared with the appropriate experimental data[17]-[32]. We have carried out calculations based on F_{SC} and F_{ISC} ; in all cases the inclusion of the term ΔF improves the agreement with the experimental data both with regard to magni-

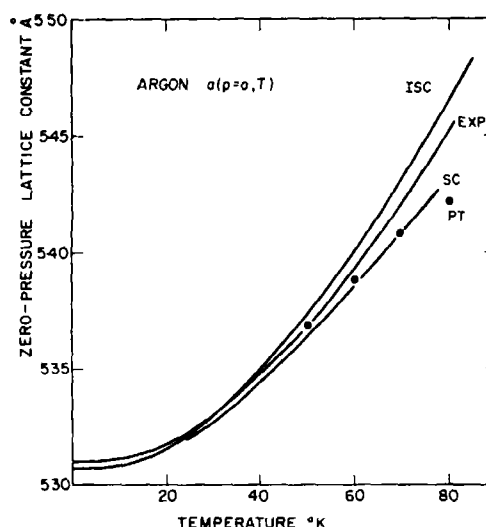


Fig. 4. Zero-pressure lattice constant of solid Ar. ISC and SC are calculated for a (12-6) Lennard-Jones potential and F_{ISC} and F_{SC} respectively. The experimental curve is taken from Ref.[18]. PT points are taken from Ref.[1].

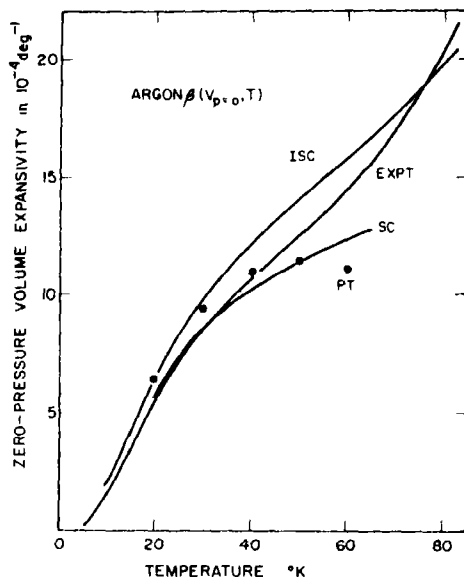


Fig. 5. Zero-pressure expansivity β of solid Ar. Caption is as in Fig. 4.

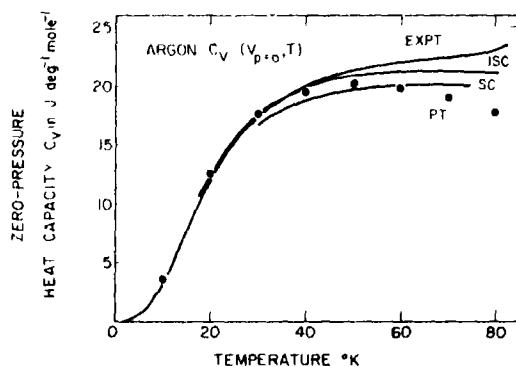


Fig. 6. Zero-pressure C_v for solid Ar. Caption as in Fig. 4 except that experimental data are from Ref. [23].

tude and temperature dependence. Results based on F_{SC} are, therefore, quoted only for Ar (Figs. 4–8). We have included some calculations based upon the quasi-harmonic approximation (QH) and conventional Born-von Kármán theory (PT) (including third and fourth order force constants in the free

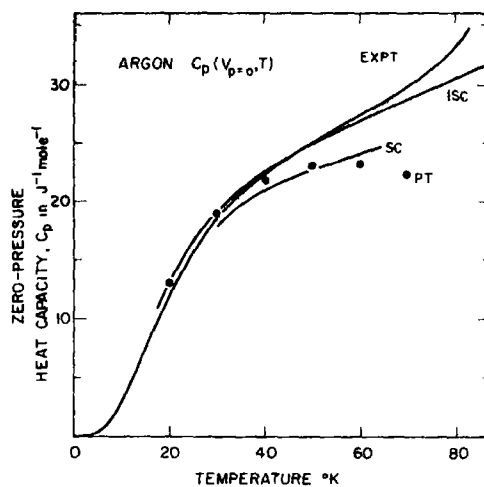


Fig. 7. Zero-pressure C_p for solid Ar. Caption as in Fig. 4 except that experimental data are from Refs. [19] and [23].

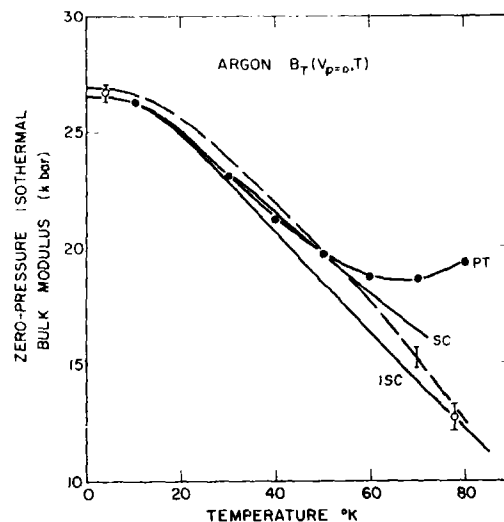


Fig. 8. Zero-pressure isothermal bulk modulus B_T of solid Ar. Caption as in Fig. 4 except that the experimental data are from Refs. [17], [18] and [21].

energy) to show to what extent these solids can be treated by conventional lattice dynamics.

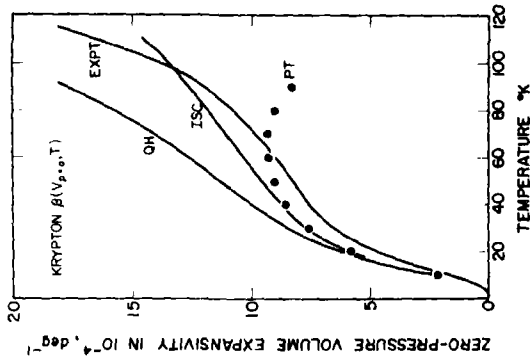


Fig. 11. Zero-pressure expansivity β , of solid Kr. Experimental data are from Ref. [22]. QH and PT are from Ref. [1]. ISC is calculated from F_{ISC} and a (12-6) potential.

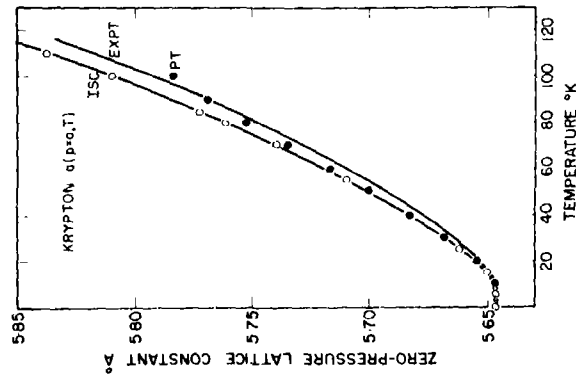


Fig. 10. Zero-pressure lattice constant of solid Kr. Experimental data are from Ref. [22]. PT is from Ref. [1] and ISC is calculated from F_{ISC} and a (12-6) potential.

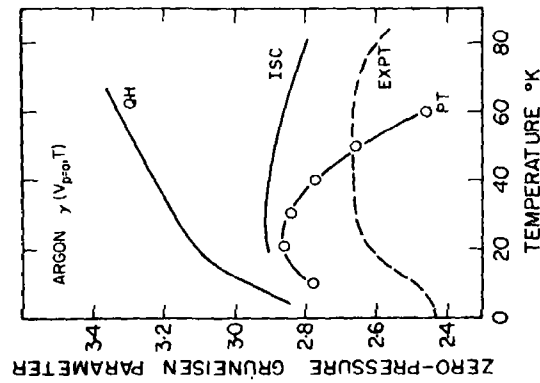


Fig. 9. Zero-pressure Grüneisen parameter of solid Ar. Caption as in Fig. 4 except that PT and QH are from Ref. [1] and experimental data are from Refs. [18] and [31].

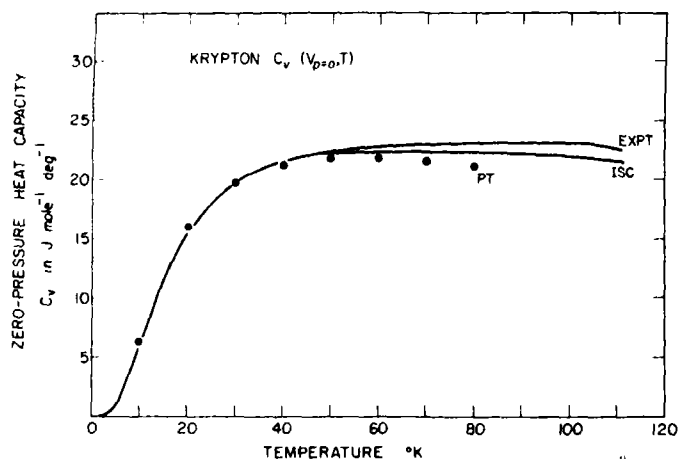


Fig. 12. Zero-pressure C_v for solid Kr. Experimental data are from Ref. [22] and [23]. PT is from Ref. [1] and ISC is calculated from F_{ISC} and a (12-6) potential.

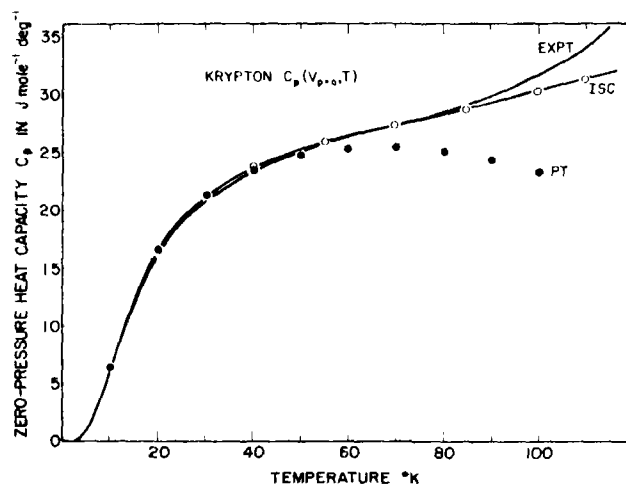


Fig. 13. Zero-pressure C_p for solid Kr. Experimental data are from Refs. [21] and [23]. PT is from Ref. [1] and ISC is calculated from F_{ISC} and a (12-6) potential.

Significant discrepancies with experiment still exist. In particular, lattice constants and expansivities appear to have too great a temperature dependence and specific heats appear to be too small at temperatures approaching melting. This point has been

especially emphasized in Fig. 22 by recent measurements of C_p at constant volume [30].

The Grüneisen parameter $\gamma = (V/C_v)\beta B_T$ provides the most stringent test of both the dynamical model (high temperatures) and the choice of inter-atomic potential (low tempera-

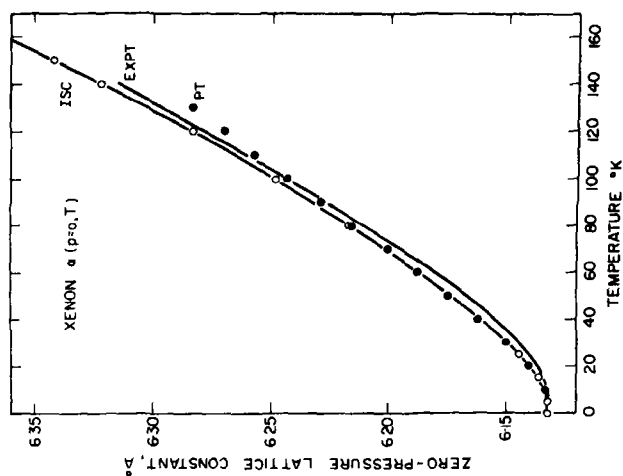


Fig. 16. Zero-pressure lattice constant for solid Xe. Experimental data are from Ref. [24]. *PT* is from Ref. [1] and *ISC* is calculated from F_{isc} and a (12-6) potential.

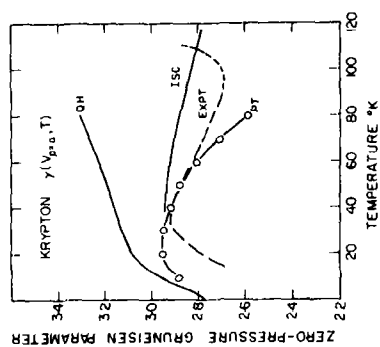


Fig. 15. Zero-pressure Grüneisen parameter for solid Kr. Experimental data are from Ref. [21] and [22]. *OH* and *PT* are from Ref. [1]. *ISC* is calculated from F_{isc} and a (12-6) potential.

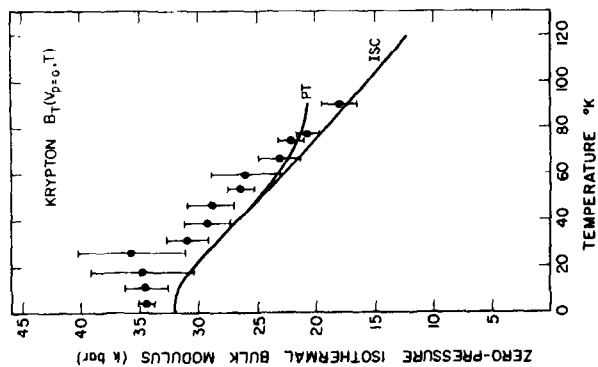


Fig. 14. Zero-pressure bulk modulus B_T of solid Kr. Experimental data are from Ref. [21]. *PT* is from Ref. [1] and *ISC* is calculated from F_{isc} and a (12-6) potential.

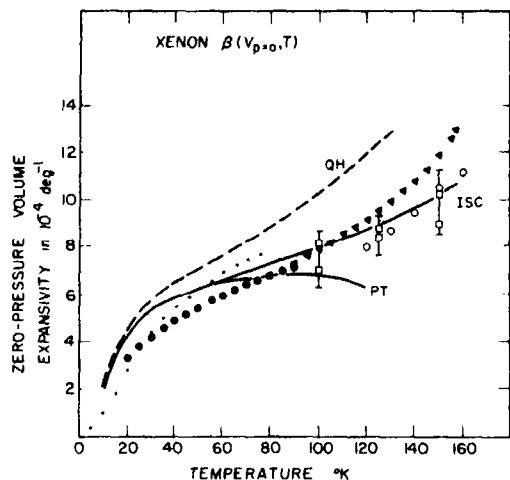


Fig. 17. Zero-pressure expansivity β for solid Xe. Various experimental data are from Refs. [24]–[28] and [32]. QH and PT are from Ref. [1]. ISC, the other solid curve, is calculated from F_{ISC} and a (12-6) potential.

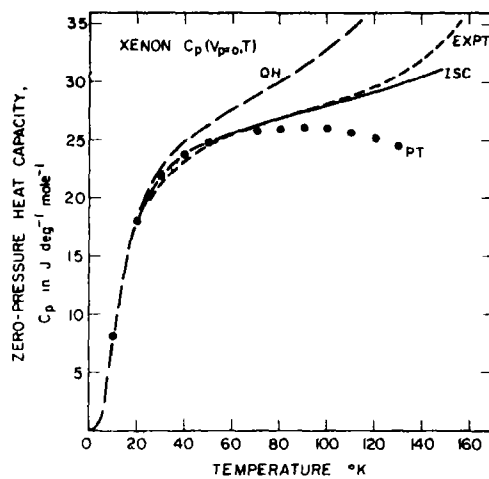


Fig. 19. Zero-pressure C_p for solid Xe. Experimental data are from Refs. [24] and [29]. QH and PT are from Ref. [1]. ISC is calculated from F_{ISC} and a (12-6) potential.

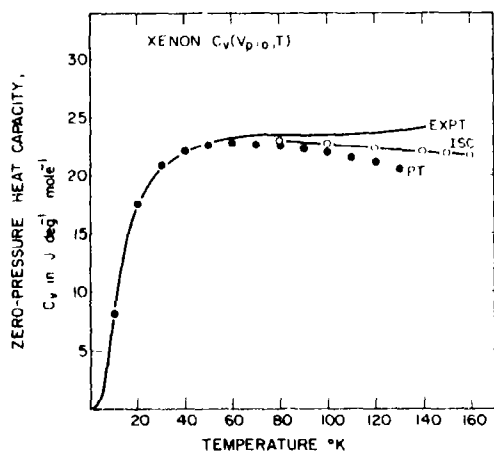


Fig. 18. Zero-pressure C_v for solid Xe. Experimental data are from Refs. [24] and [29]. PT is from Ref. [1] and ISC is calculated from F_{ISC} and a (12-6) potential.

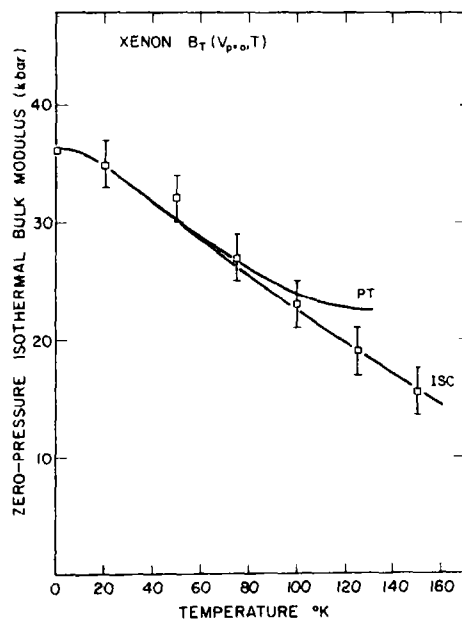


Fig. 20. Zero-pressure isothermal bulk modulus B_T for solid Xe. Experimental data are from Ref. [28]. PT is from Ref. [1] and ISC is calculated from F_{ISC} and a (12-6) potential.

tures). The failure of our Mie-Lennard-Jones central potential to reproduce the observed low temperature Grüneisen parameter for Ar has recently been stressed elsewhere [31].

Let us point out that with increasing

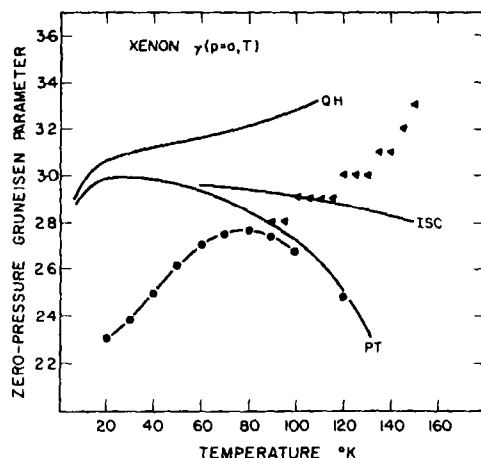


Fig. 21. Zero-pressure Grüneisen parameter for solid Xe. Experimental data are from Refs. [24] and [26] (circles) and [32] (triangles). QH and PT are from Ref.[1] and ISC is calculated from F_{ISC} and a (12-6) potential.

at higher temperatures because of the semi-perturbative nature of the method. Thus the investigation of Choquard's second order theory, in which the frequencies are renormalized, would be very fruitful.

5. CONCLUSION

We have carried out calculations of the thermodynamic properties of solid Ar, Kr and Xe based upon a short-range central potential and a self-consistent phonon scheme that includes odd-derivatives of the potential. Our present results are in far better accord with experiment than calculations based upon conventional Born-von Kármán theory. Nevertheless, as expected, our primitive potential is unable to account in detail for the whole range of properties of the heavier noble gas crystals though for some properties

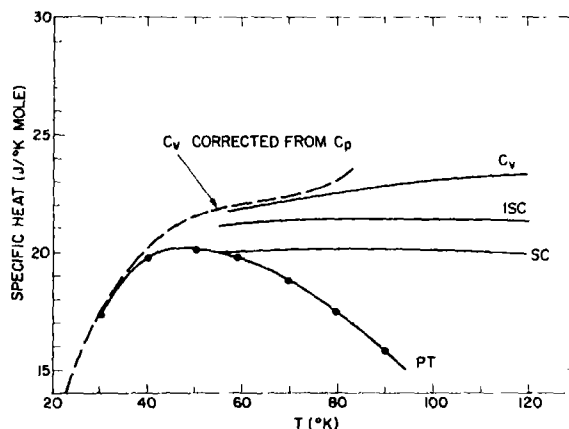


Fig. 22. C_v for Ar at a constant specific volume = 23.5 cm^3 . Experimental data from Refs. [19], [23] and [30].

temperatures an improved self consistent method becomes less reliable. This is due in part to the effects of higher order terms (4-phonon processes etc...). It is probable that the inclusion of these higher terms in a manner such as an ISC may still be inadequate and some temperature and volume ranges it

does rather well. The difficulties with the improved self consistent theory at higher temperatures are emphasized.

Acknowledgements—We would like to thank the U.S. Air Force Office of Scientific Research for their support under grant number AFOSR 68-1372. We also thank the

Rutgers Research Council for financial support. We have enjoyed several helpful discussions with Dr. Graham Chell.

REFERENCES

1. KLEIN M. L., HORTON G. K. and FELDMAN J. L., *Phys. Rev.* **184**, 968 (1969); see also FELDMAN C., KLEIN M. L. and HORTON G. K., *Phys. Rev.* **184**, 910 (1969).
2. BORN M., *Fest. Akad. Wisc., Festschrift zur feier des zweihundertjahrigen Bestehens der Akademie der Wissenschaften in Göttingen: I Mathematische-physikalische Klasse* (Springer-Verlag, Berlin) (1951).
3. HOOTON D. J., *Phil. Mag.* **46**, 422 (1955); **46**, 433 (1955).
4. CHOQUARD P. F., *The Anharmonic Crystal* Benjamin, New York (1967).
5. KOEHLER T. R., *Phys. Rev.* **144**, 789 (1966); *Phys. Rev. Lett.* **17**, 89 (1966) and **22**, 777 (1969).
6. PLAKIDA N. M. and SIKLOS T., *Acta phys. hung* **25**, 17 (1968).
7. BOCCARA N. and SARMA G., *Physics* **1**, 219 (1965); see also RANINGER J., *Phys. Rev.* **140A**, 2031 (1965).
8. HORNER H., *Z. Phys.* **205**, 72 (1967).
9. GILLIS N. S., WERTHAMER N. R. and KOEHLER T. R., *Phys. Rev.* **165**, 95 (1968).
10. GOLDMAN V. V., HORTON G. K. and KLEIN M. L., *Phys. Rev. Lett.* **21**, 1527 (1968), *Phys. Lett.* **28A**, 341 (1968).
11. GOLDMAN V. V., HORTON G. K. and KLEIN M. L., *J. low temp. Phys.* **5**, 391 (1969).
12. KOEHLER T. R., *Phys. Rev. Lett.* **22**, 777 (1969).
13. KLEIN M. L., KEIL T. H., GOLDMAN V. V. and HORTON G. K., *J. Phys. C.: Solid State Phys.* **3**, 33 (1970).
14. KLEIN M. L., BLIZARD W. and GOLDMAN V. V., *J. chem. Phys.* (To be published).
15. See for example, BARKER J. A. and POMPE A., *Aust. J. Chem.* **21**, 1683 (1968).
16. HORTON G. K., *Am. J. Phys.* **36**, 93 (1968).
17. KEELER G. and BATCHELDER D. N., *J. Phys. C.: Solid State Phys.* **3**, 510 (1970).
18. PETERSON O. G., BATCHELDER D. N. and SIMMONS R. O., *Phys. Rev.* **150**, 703 (1966).
19. FINEGOLD L. and PHILLIPS N. E., *Phys. Rev.* **177**, 1383 (1969).
20. FLUBACHER P., LEADBETTER A. J. and MORRISON J. A., *Proc. phys. Soc. Lond.* **78**, 1449 (1961).
21. URVAS A. O., LOSEE D. L. and SIMMONS R. O., *J. Phys. Chem. Solids* **28**, 2269 (1967).
22. LOSEE D. L. and SIMMONS R. O., *Phys. Rev.* **173**, 873 (1968).
23. BEAUMONT R. H., CHIHARA H. and MORRISON J., *Proc. phys. Soc. Lond.* **78**, 1462 (1961).
24. Compilation of available data on Xe due to J. U. Trefny Ph.D. thesis Rutgers University 1968. See also SERIN B., and TREFNY J., *J. low temp. Phys.* **1**, 23 (1969).
25. SEARS D. R. and KLUG H. P., *J. chem. Phys.* **37**, 3022 (1962).
26. MANZHELII V. G., GRAVILKO V. G. and BOILOVICH E. I., *Soviet Phys. solid St.* **9**, 1157 (1967).
27. GRAVILKO V. G. and MANZHELII V. G., *Soviet Phys. solid St.* **6**, 1734 (1964).
28. PACKARD J. R. and SWENSON C. A., *J. Phys. Chem. Solids* **24**, 1405 (1963).
29. FENICHEL H. and SERIN B., *Phys. Rev.* **142**, 490 (1966).
30. HAENSSLER F., GAMPER K. and SERIN B., *J. low temp. Phys.* (To be Published).
31. TILFORD C. R. and SWENSON C. A., *Phys. Rev. Lett.* **22**, 1296 (1969).
32. MANZHELII V. G., GRAVILKO V. G. and KUCHNEV V. I., *Phys. Status Solidi* **34**, K55 (1969).

PHONON-INDUCED HOPPING TRANSITIONS IN GERMANIUM AND SILICON

ANDRZEJ MYSZKOWSKI

Institute of Physics, Polish Academy of Sciences, Warsaw, Poland

(Received 23 December 1969)

Abstract—The probability of the phonon-induced electron transitions is basic for the theories of the hopping phenomena in Ge and Si at very low temperatures. Myszkowski and Rogala obtained the probability of the two-donor transitions using the adiabatic approximation and the approximation of the weak electron-lattice interaction. Both donor centers were assumed to be on substitutional sites in the same sublattice of the diamond-type crystal. Here the theory is extended to the case of the donor centers on arbitrary substitutional sites and, also, the previous approximations are discussed. The transition probability is a rapidly-oscillating function of the donor positions. The performed average over small regions around each of the actual positions of the donor centers does not have the oscillating behaviour and will be convenient in practical applications, i.e. in the theories of the macroscopic phenomena, e.g. hopping conductivity.

1. INTRODUCTION

MANY electrical[1-13] and optical[14-16] phenomena in Ge and Si crystals at very low temperatures are conditioned by hopping processes. These phenomena are observed in the crystals of Ge and Si lightly doped with the impurities of both kinds, i.e. donors and acceptors. We consider only the *n*-type materials with the concentration of donors N_d higher than the concentration of acceptors N_a . Then the N_a electrons introduced by the donor centers occupy all the acceptor centers. Therefore, only $N_d - N_a$ donors are neutral. At sufficiently low temperatures the electrons on the donor centers are not excited to the conduction band. If the concentration of donors is sufficiently low then the overlaps of one-center wave functions are small and the donor states are localized. These states have different energies because the randomly-distributed acceptor centers produce local electric fields. Moreover, the interaction splits the states. Some of these states are ionized and some neutral; therefore, the electron transitions are possible. They are accompanied by absorption or emission of photons or phonons and called the 'hopping

transitions'. In this paper we are interested only in the phonon hopping transitions.

The simplest microscopic model of the hopping transitions was given by Miller and Abrahams[6]. These authors considered the system of two donor centers and one electron in an external, static electric field. The wave functions of the electron in the two lowest states were assumed as the linear combinations of the one-center wave functions. Miller and Abrahams used the variational procedure and obtained the coefficients of these combinations and the energy difference between the two lowest states. The distance between the centers of a pair was assumed to be sufficiently large. Both centers of the donor pair were assumed to occupy substitutional sites. This assumption is satisfied by the Group-V donors. Moreover, the authors assumed that both centers of the donor pair belong to the same sublattice. This assumption cannot be justified for randomly distributed donor centers. In this respect, the theory of Miller and Abrahams is incomplete. Moreover, the probability of the transition process between the two-center states was calculated too crudely, on the basis of the simplest Born-Hartree approximation.

Gummel and Lax[17] gave the general formalism of the transition probability between two nondegenerate electron states with simultaneous absorption or emission of phonons. They used the more appropriate adiabatic approximation of Born and Oppenheimer. Moreover, they assumed the electron-lattice interaction to be weak and the perturbing operator to be linear in the amplitude of the phonon wave.

The general Gummel-Lax formalism was applied in paper of Myszkowski and Rogala [18] (hereafter referred to as 1). The authors considered the electron-lattice interaction in Ge and Si crystals. The wave functions of the electron were assumed in a general form. The perturbing phonon operator was determined on the basis of the deformation potential theory. The two independent deformation potential constants were taken into account, which was one of the main purposes of that paper. The model of an isotropic continuous medium was used for the phonon spectrum of the crystal. The longitudinal as well as the transverse acoustic phonons were taken into account. Under these assumptions the authors obtained the general formulas for the phonon distribution functions, which determine the transition probability. Moreover, Myszkowski and Rogala considered the energy of the interaction of an electron with the crystal lattice. We quote the general formulas of the transition probability in Section 2 and, subsequently, use them in Section 4 to consider the case of donor centers on arbitrary substitutional sites.

In paper 1 the authors applied their general formulas and the two-center wave functions given by Miller and Abrahams to obtain the transition probability between the two-center donor states. Only the processes with simultaneous absorption or emission of one phonon were considered. To simplify the calculations the potential of the external electric field was assumed to be approximately linear in the region of the centers. The calculations were performed effectively only for the two par-

ticular cases: 'high frequency' and 'low frequency' case. However, the general Gummel-Lax assumptions of the adiabatic character of the process and of the weak electron-phonon interaction were not discussed for the two-center transitions. The authors calculated also the electron-lattice interaction energy E_{LR} for electron bound to one donor center in the lowest state.

The purposes of our work are the following. We discuss the assumptions used in paper 1 in the transition probability formalism and we generalize the results of that paper to the case of the arbitrary substitutional positions of the donor centers. Moreover, we average the transition probability over the actual positions of the donor centers to eliminate its oscillating component.

In Section 3 we discuss the transformation of the one-center wave function induced by the displacement of the donor center from the first sublattice of the crystal to the second. The obtained results are used subsequently to generalize the procedure of Miller and Abrahams to the case of donor centers on arbitrary substitutional sites.

In Section 4 we quote the results of paper 1 for the electron-lattice interaction energy. Here only the lowest, singlet one-center state of the electron is considered. Then these results are used to obtain the wave number of phonons which interact most strongly with the electron bound to the donor center. In the following part of this section we quote the formulas of the transition probability obtained in paper 1, both in the 'high frequency' and 'low frequency' cases. We discuss the simplifying assumptions used in paper 1. In particular, the resulting upper limit for the temperature of the crystal. The previous results concerning the most strongly coupled phonons are used to obtain the adiabatic condition for the two-center transitions. Moreover, we use the value of E_{LR} given in paper 1 to obtain the condition of the weak electron-phonon interaction. Both obtained conditions restrict considerably the applica-

bility of the 'low frequency' case. On the other hand, these conditions are well satisfied in the 'high frequency' case. Using the two-center wave functions of Section 3 in the general formulas of Section 2 we obtain the transition probability in the case of the donor centers on opposite substitutional sites. It is of similar form as in the previous case (donor centers in the same sublattice).

The transition probability depends on the distance between the donor centers $\mathbf{R}$, being a rapidly-oscillating function of it (the oscillating period is comparable with the lattice constant). However, the formulas for the transition probability is used in practice to obtain some macroscopic effects. In these effects a very large number of donor pairs in the crystal is involved. Therefore, the oscillating behaviour of the transition probability is unimportant. Thus, we perform the approximate average of the transition probability, both in the 'high frequency' and 'low frequency' cases. We consider separately the cases of the centers being on substitutional sites of the same sublattice and on opposite substitutional sites. The obtained formulas are slowly-varying functions of $\mathbf{R}$ and are of the same form for both possible arrangements of the centers. They are convenient in practical applications, i.e. in the theories of the macroscopic hopping phenomena, e.g. the impurity conduction in the hopping region.

2. GENERAL FORMALISM

Gummel and Lax[17] gave the general formalism for the electron transitions induced by a weak phonon perturbation. They used the adiabatic Born-Oppenheimer approximation. The probability of the electron transition from the state a to the state b with simultaneous absorption or emission of only one phonon of the frequency ω_0 is

$$W_{ba}^{(1)} = 2\pi\hbar^{-2} \exp(-\alpha) [h(\omega_0) - \gamma^* g(\omega_0) - \gamma g^*(\omega_0) + |\gamma|^2 f(\omega_0)], \quad (2.1)$$

where

$$\alpha = \int_{-\infty}^{+\infty} f(\omega) d\omega, \quad (2.2)$$

$$\gamma = \int_{-\infty}^{+\infty} g(\omega) d\omega. \quad (2.3)$$

Here ω is the phonon frequency. Positive frequencies correspond to the emission and negative frequencies to the absorption of a phonon.

The functions $h(\omega)$ and $g(\omega)$ are the distribution functions of so-called 'kinetic phonons'. These phonons arise because the energies of the electron states are different. Here the equilibrium positions of the crystal atoms are considered to be unaffected by the state of the electron. The function $f(\omega)$ is connected with 'lattice relaxation' phonons. These phonons arise because of a local deformation of the crystal around the electron. This deformation consists of a displacement of the equilibrium positions of the crystal atoms. The electron transition from one state to another may, therefore, induce a motion of the crystal lattice. Hence, emission or absorption of a phonon is possible. The one-phonon transitions, considered here, play a dominant role if $\alpha \ll 1$ [19-21].

ω_0 is the frequency conserving the total energy of the system, being the sum of two terms. The first term is the difference of the energy between the two electron states in nondeformed crystal lattice. The other term is the difference of the electron-lattice interaction energy in these states. Because the second term is very small (of the order of magnitude of $E_{LH} \cdot S$) [14] for the two-center donor states (which are considered in this paper) it can be neglected. Then we have

$$\hbar\omega_0 \approx E_a(0) - E_b(0) = \Delta E_{ba}, \quad (2.4)$$

where $E_a(0)$ and $E_b(0)$ are the energies of the electron in the states a and b , respectively, in nondeformed crystal lattice. The extension of that formalism on the non-adiabatic processes was done by Takeyama[21].

In paper 1 the general Gummel-Lax formalism was applied to the problem of the interaction of electrons with the acoustical phonons (both longitudinal and transverse) in Ge and

Si crystals. The wave functions of the electron states were assumed in the general form

$$u_a(\mathbf{r}) = n^{-1/2} \sum_{i=1}^n F_a^{(i)}(\mathbf{r}) \Phi^{(i)}(\mathbf{r}), \quad (2.5)$$

and

$$u_b(\mathbf{r}) = n^{-1/2} \sum_{i=1}^n F_b^{(i)}(\mathbf{r}) \Phi^{(i)}(\mathbf{r}). \quad (2.6)$$

Here $\Phi^{(i)}(\mathbf{r})$ is the Bloch function corresponding to the i -th minimum of the conduction

band. The functions $F_a^{(i)}(\mathbf{r})$ and $F_b^{(i)}(\mathbf{r})$ change slowly as compared with the Bloch functions. The sum is performed over all the minima of the conduction band (4 for Ge, 6 for Si). The crystal temperature was assumed to be very low as compared with the Debye temperature. This makes possible to approximate the acoustical phonon spectrum by the spectrum of an isotropic continuous medium. Under these assumptions the distribution functions were obtained in the form

$$\begin{aligned} f(\omega) = & \theta(\omega) (16\pi^3 \hbar n^2 d)^{-1} \sum_{i,j=1}^n \int \left\{ v_L^{-5} [\Xi_d + \Xi_u(\mathbf{k}^{(i)} \cdot \boldsymbol{\Omega})^2] [\Xi_d + \Xi_u(\mathbf{k}^{(j)} \cdot \boldsymbol{\Omega})^2] \right. \\ & \times \left[\left\langle F_b^{(i)}(\mathbf{r}) \right| \exp\left(i \frac{|\boldsymbol{\omega}|}{v_L} \boldsymbol{\Omega} \cdot \mathbf{r}\right) \left| F_b^{(j)}(\mathbf{r}) \right\rangle - \left\langle F_a^{(i)}(\mathbf{r}) \right| \exp\left(i \frac{|\boldsymbol{\omega}|}{v_L} \boldsymbol{\Omega} \cdot \mathbf{r}\right) \left| F_a^{(j)}(\mathbf{r}) \right\rangle \right] \\ & \times \left[\left\langle F_b^{(j)}(\mathbf{r}) \right| \exp\left(-i \frac{|\boldsymbol{\omega}|}{v_L} \boldsymbol{\Omega} \cdot \mathbf{r}\right) \left| F_b^{(i)}(\mathbf{r}) \right\rangle - \left\langle F_a^{(j)}(\mathbf{r}) \right| \exp\left(-i \frac{|\boldsymbol{\omega}|}{v_L} \boldsymbol{\Omega} \cdot \mathbf{r}\right) \left| F_a^{(i)}(\mathbf{r}) \right\rangle \right] \\ & + v_T^{-5} \Xi_u^2(\mathbf{k}^{(i)} \cdot \boldsymbol{\Omega})(\mathbf{k}^{(j)} \cdot \boldsymbol{\Omega}) [(\mathbf{k}^{(i)} \cdot \mathbf{k}^{(j)}) - (\mathbf{k}^{(i)} \cdot \boldsymbol{\Omega})(\mathbf{k}^{(j)} \cdot \boldsymbol{\Omega})] \\ & \times \left[\left\langle F_b^{(i)}(\mathbf{r}) \right| \exp\left(i \frac{|\boldsymbol{\omega}|}{v_T} \boldsymbol{\Omega} \cdot \mathbf{r}\right) \left| F_b^{(i)}(\mathbf{r}) \right\rangle - \left\langle F_a^{(i)}(\mathbf{r}) \right| \exp\left(i \frac{|\boldsymbol{\omega}|}{v_T} \boldsymbol{\Omega} \cdot \mathbf{r}\right) \left| F_a^{(i)}(\mathbf{r}) \right\rangle \right] \\ & \times \left[\left\langle F_b^{(j)}(\mathbf{r}) \right| \exp\left(-i \frac{|\boldsymbol{\omega}|}{v_T} \boldsymbol{\Omega} \cdot \mathbf{r}\right) \left| F_b^{(j)}(\mathbf{r}) \right\rangle \right. \\ & \left. \left. - \left\langle F_a^{(j)}(\mathbf{r}) \right| \exp\left(-i \frac{|\boldsymbol{\omega}|}{v_T} \boldsymbol{\Omega} \cdot \mathbf{r}\right) \left| F_a^{(j)}(\mathbf{r}) \right\rangle \right] \right\} d\boldsymbol{\Omega}, \quad (2.7) \end{aligned}$$

$$\begin{aligned} g(\omega) = & -\theta(\omega) \hbar \omega^2 [32\pi^3 n^2 (E_b(0) - E_a(0)) d]^{-1} \sum_{i,j=1}^n \int \left(v_L^{-5} [\Xi_d + \Xi_u(\mathbf{k}^{(i)} \cdot \boldsymbol{\Omega})^2] \right. \\ & \times [\Xi_d + \Xi_u(\mathbf{k}^{(j)} \cdot \boldsymbol{\Omega})^2] \left\{ \left[\left\langle F_b^{(i)}(\mathbf{r}) \right| \exp\left(i \frac{|\boldsymbol{\omega}|}{v_L} \boldsymbol{\Omega} \cdot \mathbf{r}\right) \left| F_b^{(j)}(\mathbf{r}) \right\rangle \right. \right. \\ & \left. \left. - \left\langle F_a^{(i)}(\mathbf{r}) \right| \exp\left(i \frac{|\boldsymbol{\omega}|}{v_L} \boldsymbol{\Omega} \cdot \mathbf{r}\right) \left| F_a^{(j)}(\mathbf{r}) \right\rangle \right] \left[\left\langle F_b^{(j)}(\mathbf{r}) \right| \exp\left(-i \frac{|\boldsymbol{\omega}|}{v_L} \boldsymbol{\Omega} \cdot \mathbf{r}\right) \left| F_a^{(i)}(\mathbf{r}) \right\rangle \right. \right. \\ & \left. \left. + \left[\left\langle F_b^{(j)}(\mathbf{r}) \right| \exp\left(-i \frac{|\boldsymbol{\omega}|}{v_L} \boldsymbol{\Omega} \cdot \mathbf{r}\right) \left| F_b^{(i)}(\mathbf{r}) \right\rangle - \left\langle F_a^{(j)}(\mathbf{r}) \right| \exp\left(-i \frac{|\boldsymbol{\omega}|}{v_L} \boldsymbol{\Omega} \cdot \mathbf{r}\right) \left| F_a^{(i)}(\mathbf{r}) \right\rangle \right] \right\} \\ & \times \left\langle F_b^{(i)}(\mathbf{r}) \right| \exp\left(i \frac{|\boldsymbol{\omega}|}{v_L} \boldsymbol{\Omega} \cdot \mathbf{r}\right) \left| F_a^{(i)}(\mathbf{r}) \right\rangle \left\{ + v_T^{-5} \Xi_u^2(\mathbf{k}^{(j)} \cdot \boldsymbol{\Omega})(\mathbf{k}^{(i)} \cdot \boldsymbol{\Omega}) \right. \\ & \times [(\mathbf{k}^{(i)} \cdot \mathbf{k}^{(j)}) - (\mathbf{k}^{(i)} \cdot \boldsymbol{\Omega})(\mathbf{k}^{(j)} \cdot \boldsymbol{\Omega})] \left\{ \left[\left\langle F_b^{(i)}(\mathbf{r}) \right| \exp\left(i \frac{|\boldsymbol{\omega}|}{v_T} \boldsymbol{\Omega} \cdot \mathbf{r}\right) \left| F_b^{(i)}(\mathbf{r}) \right\rangle \right. \right. \\ & \left. \left. - \left\langle F_a^{(i)}(\mathbf{r}) \right| \exp\left(i \frac{|\boldsymbol{\omega}|}{v_T} \boldsymbol{\Omega} \cdot \mathbf{r}\right) \left| F_a^{(i)}(\mathbf{r}) \right\rangle \right] \left[\left\langle F_b^{(j)}(\mathbf{r}) \right| \exp\left(-i \frac{|\boldsymbol{\omega}|}{v_T} \boldsymbol{\Omega} \cdot \mathbf{r}\right) \left| F_a^{(j)}(\mathbf{r}) \right\rangle \right. \right. \\ & \left. \left. + \left[\left\langle F_b^{(j)}(\mathbf{r}) \right| \exp\left(-i \frac{|\boldsymbol{\omega}|}{v_T} \boldsymbol{\Omega} \cdot \mathbf{r}\right) \left| F_b^{(j)}(\mathbf{r}) \right\rangle - \left\langle F_a^{(j)}(\mathbf{r}) \right| \exp\left(-i \frac{|\boldsymbol{\omega}|}{v_T} \boldsymbol{\Omega} \cdot \mathbf{r}\right) \left| F_a^{(j)}(\mathbf{r}) \right\rangle \right] \right\} \right\} d\boldsymbol{\Omega} \end{aligned}$$

$$\begin{aligned}
 & + \left[\left\langle F_b^{(j)}(\mathbf{r}) \right| \exp \left(-i \frac{|\omega|}{v_T} \mathbf{\Omega} \cdot \mathbf{r} \right) \right| F_b^{(j)}(\mathbf{r}) \rangle - \left\langle F_a^{(j)}(\mathbf{r}) \right| \exp \left(-i \frac{|\omega|}{v_T} \mathbf{\Omega} \cdot \mathbf{r} \right) \right| F_a^{(j)}(\mathbf{r}) \rangle \right] \\
 & \times \left\langle F_b^{(i)}(\mathbf{r}) \right| \exp \left(i \frac{|\omega|}{v_T} \mathbf{\Omega} \cdot \mathbf{r} \right) \right| F_a^{(i)}(\mathbf{r}) \rangle \Bigg\} d\Omega, \quad (2.8)
 \end{aligned}$$

$$\begin{aligned}
 h(\omega) = & \theta(\omega) \hbar^3 \omega^4 [16\pi^3 n^2 (E_b(0) - E_a(0))^2 d]^{-1} \sum_{i,j=1}^n \int \left\{ v_L^{-5} [\Xi_d + \Xi_u(\mathbf{k}^{(i)} \cdot \mathbf{\Omega})^2] \right. \\
 & \times [\Xi_d + \Xi_u(\mathbf{k}^{(j)} \cdot \mathbf{\Omega})^2] \left\langle F_b^{(i)}(\mathbf{r}) \right| \exp \left(i \frac{|\omega|}{v_L} \mathbf{\Omega} \cdot \mathbf{r} \right) \right| F_a^{(i)}(\mathbf{r}) \rangle \\
 & \times \left\langle F_a^{(j)}(\mathbf{r}) \right| \exp \left(-i \frac{|\omega|}{v_L} \mathbf{\Omega} \cdot \mathbf{r} \right) \right| F_b^{(j)}(\mathbf{r}) \rangle + v_T^{-5} \Xi_u^2(\mathbf{k}^{(i)} \cdot \mathbf{\Omega})(\mathbf{k}^{(j)} \cdot \mathbf{\Omega}) \\
 & \times [(\mathbf{k}^{(i)} \cdot \mathbf{k}^{(j)}) - (\mathbf{k}^{(i)} \cdot \mathbf{\Omega})(\mathbf{k}^{(j)} \cdot \mathbf{\Omega})] \left\langle F_b^{(i)}(\mathbf{r}) \right| \exp \left(i \frac{|\omega|}{v_T} \mathbf{\Omega} \cdot \mathbf{r} \right) \right| F_a^{(i)}(\mathbf{r}) \rangle \\
 & \times \left\langle F_a^{(j)}(\mathbf{r}) \right| \exp \left(-i \frac{|\omega|}{v_T} \mathbf{\Omega} \cdot \mathbf{r} \right) \right| F_b^{(j)}(\mathbf{r}) \rangle \Bigg\} d\Omega, \quad (2.9)
 \end{aligned}$$

where

$$\theta(\omega) = [2 \sin \hbar(\hbar\omega/2kT)]^{-1} \omega \exp(\hbar\omega/2kT). \quad (2.10)$$

Here Ξ_d and Ξ_u are the deformation potential constants, v_L and v_T the velocities of the longitudinal and transverse phonon waves, respectively, d is the crystal density, T is the temperature of the crystal. $\mathbf{k}^{(i)}$ is the unit vector of the direction from the center of the Brillouin zone to the i -th minimum of the conduction band. The integration is performed over all the directions of the phonon wave vector $\tau = (|\omega|/v)\mathbf{\Omega}$. $\mathbf{\Omega}$ is a unit vector of the direction of τ .

The formulas (2.7–2.10) can be applied to arbitrary electron states in Ge and Si, if their wave functions are of the form (2.5) and (2.6). In particular, we are interested here in the two-center donor states in the case of arbitrary substitutional positions of the centers.

3. ELECTRONIC STATES

(a) One-center states

The lowest state of an electron, bound to

an isolated shallow donor center in Ge or Si, is the singlet state. It results from the effect of the 'chemical shift' potential (short-range potential being the difference between the donor ion potential and the Coulombic potential). The wave function of that state was found in the form [22]

$$u(\mathbf{r}) = n^{-1/2} \sum_{i=1}^n F^{(i)}(\mathbf{r}) \Phi^{(i)}(\mathbf{r}), \quad (3.1)$$

where the envelope $F^{(i)}(\mathbf{r})$ is given by

$$F^{(i)}(\mathbf{r}) = (\pi a^2 b)^{-1/2} \exp(-\mathbf{r}_i/a). \quad (3.2)$$

$$\mathbf{r}_i = a[(x_i^2 + y_i^2)/a^2 + z_i^2/b^2]^{1/2}. \quad (3.3)$$

The ' z_i ' axis is parallel to the axis containing the i -th minimum, i.e. to $\mathbf{k}^{(i)}$. The constants a and b are the perpendicular and longitudinal radii of the orbit, respectively. Their values for Ge and Si are given in Table 1. They are much larger than the lattice constants. Therefore, the envelopes $F^{(i)}(\mathbf{r})$ change slowly in each elementary cell.

The crystal lattice of Ge and Si has a two-atomic basis and can be viewed as two face-centered cubic sublattices, penetrating each

Table 1. Material constants

Material	d (g/cm ³)	v_L (10 ⁸ cm/sec)	v_T (10 ⁸ cm/sec)	Ξ_d (eV)	Ξ_u (eV)	γ	a (Å)	E_{LR} (meV)
Ge	5.4	5.4 ^a	3.2 ^a	-10.9 ^{b,c,d}	16.2 ^c	0.9495 ^e	70.8 ^e	0.0033
Si	2.3	9.2 ^a	5.4 ^a	2.6 ^{c,d,f}	8.6 ^c	0.8077 ^e	22.1 ^e	0.13

^aSAMOILOVICH A. G. and ISKRA V. D., *Fiz. tverd. Tela* 2, 2827 (1960) (English transl: *Soviet Phys. solid St.* 2, 2517 (1961)).

^bBAGGULEY D. M. S., FLAXEN D. W. and STRADLING R. A., *Phys. Lett.* 1, 111 (1962).

^cBALSLEV I., *Phys. Rev.* 143, 636 (1966).

^dObtained from the ratio Ξ_d/Ξ_u .

^eSee Ref. [29].

^fKoenig (private communication). See SHAM L. J., *Proc. phys. Soc. Lond.* 81, 934 (1963).

other. All sites in a given sublattice are equivalent each to the other. Therefore, we can limit our considerations only to the two cases: the impurity atom replacing the first or the second atom of the basis in a given elementary cell. For convenience, we assume the origin of the coordinate system at the position of the first atom of the basis. If just this atom is replaced by the impurity ion, the wave function is of the well-known form (3.1). The other case has not been considered up till now. It can be obtained from the first case by an operation exchanging the atoms of the basis. Such operation is the space inversion connected with fractional translation $\mathbf{t}$. Thus, in the second case, we can obtain the wave function of the electron on the basis of the formula (3.1). It yields

$$\bar{u}(\mathbf{r}-\mathbf{t}) = \{I/\mathbf{t}\} u(\mathbf{r}) = n^{-1/2} \sum_{i=1}^n F^{(i)}(-\mathbf{r}+\mathbf{t}) \times \{I/\mathbf{t}\} \Phi^{(i)}(\mathbf{r}). \quad (3.4)$$

The Bloch functions $\Phi^{(i)}(\mathbf{r})$ are eigenfunctions of the Hamiltonian of the ideal crystal. This Hamiltonian is invariant under the symmetry operation $\{I/\mathbf{t}\}$. Transforming the Bloch functions we obtain

$$\{I/\mathbf{t}\} \Phi^{(i)}(\mathbf{r}) = \exp(-\frac{1}{2}\pi i) \exp(i\mathbf{t} \cdot \mathbf{p}^{(i)}) \Phi^{(i)}(\mathbf{r}) \quad (3.5)$$

for Ge and

$$\{I/\mathbf{t}\} \Phi^{(i)}(\mathbf{r}) = \exp(i\mathbf{t} \cdot \mathbf{p}^{(i)}) \Phi^{(j)}(\mathbf{r}) \quad (3.6)$$

for Si. Here $\mathbf{p}^{(i)}$ is the vector from the center of the Brillouin zone to the i -th minimum of the conduction band. In the case of Ge the four vectors $\mathbf{p}^{(i)}$ are chosen in the directions of the nonprimitive translations $\mathbf{t}^{(i)}$ which transform the first sublattice to the second sublattice, so that $\mathbf{p}^{(i)} \cdot \mathbf{t}^{(i)} = \frac{1}{2}\pi$. The subscript j in equation (3.6) corresponds to $\mathbf{p}^{(j)} = -\mathbf{p}^{(i)}$. For the orbitals (3.2) are invariant under the space inversion we obtain on the basis of equations (3.4-3.6)

$$\bar{u}(\mathbf{r}-\mathbf{t}) = n^{-1/2} \exp(-\frac{1}{2}\pi i) \sum_{i=1}^n F^{(i)}(\mathbf{r}-\mathbf{t}) \times \Phi^{(i)}(\mathbf{r}) \exp(i\mathbf{t} \cdot \mathbf{p}^{(i)}) \quad (3.7)$$

for Ge and

$$\bar{u}(\mathbf{r}-\mathbf{t}) = n^{-1/2} \sum_{i=1}^n F^{(i)}(\mathbf{r}-\mathbf{t}) \Phi^{(i)}(\mathbf{r}) \exp(-i\mathbf{t} \cdot \mathbf{p}^{(i)}) \quad (3.8)$$

for Si. These are the wave functions of the electron bound to the donor ion at the 'second' site of the basis. Here the origin of the coordinate system is still at the first site of the basis. Now we shift the origin of the coordinate system to the position of the impurity atom (i.e. to the 'second' site of the basis, so that $\mathbf{r}' = \mathbf{r}-\mathbf{t}$). Thus, for Ge we obtain

$$\bar{u}(\mathbf{r}') = n^{-1/2} \exp(-\frac{1}{2}\pi i) \sum_{i=1}^n F^{(i)}(\mathbf{r}') \Phi^{(i)}(\mathbf{r}'+\mathbf{t}) \exp(i\mathbf{t} \cdot \mathbf{p}^{(i)}) \quad (3.9)$$

and for Si

$$\begin{aligned} \tilde{u}(\mathbf{r}') \\ = n^{-1/2} \sum_{\mathbf{t}} F^{(0)}(\mathbf{r}') \Phi^{(0)}(\mathbf{r}' + \mathbf{t}) \exp(-i\mathbf{t} \cdot \mathbf{p}^{(0)}). \end{aligned} \quad (3.10)$$

These functions are represented by the same system of the Bloch functions as the wave function (3.1) (in both cases the Bloch functions are centered at the first site of the basis). This representation is convenient in many-center problems which involve calculations of matrix elements between different one-center functions. If the centers of the system do not belong to the same sublattice then the functions (3.9) or (3.10) should be used together with the function (3.1). In our paper we use the functions (3.9) and (3.10) in the next section concerning the two-center states.

Here we obtain the one-center singlet wave function corresponding to the donor center at the 'second' site in the basis. However, the present method can be applied also to other one-center functions. In the next paper[23] we discuss the one-center wave function in the presence of an external magnetic field.

(b) Two-center states

Let us consider the system of the two donor ions and one electron in Ge or Si crystal in an external electric field. Miller and Abrahams [6] solved this problem by a variational procedure, assuming a sufficiently large distance between the centers. They obtained the wave functions of the electron in the two lowest states as linear combinations of the one-center singlet wave functions. The corrections due to the higher one-center states can be neglected because of the 'chemical shift' splitting. This splitting is much higher than the difference of the energy between the two-center states.

The variational procedure of Takeyama *et al.*[24] leads to another two-center wave functions which are incorrect. The trial functions were assumed as the linear combinations

of the orbitals with the same direction of the 'z_i' axis. These orbitals were centered on the first and the second donor center, respectively. The authors obtained the coefficients of the linear combinations and the energy separation between the states. The energy splitting of the states appeared because the direction from one center to the other distinguishes the orbitals. After that the authors discussed the influence of the 'chemical shift' potential. As a matter of fact, this potential splits the states stronger[25-28]. Because of that the 'chemical shift' potential should be taken into account at an earlier stage to choose correctly the trial functions. The correct trial functions were assumed by Miller and Abrahams. They used the one-center singlet wave functions including the contributions from all the conduction band minima. Moreover, Takeyama *et al.* assumed that their trial functions diagonalize the 'chemical shift' potential. However, the assumption that the off-diagonal matrix element are negligible is in contradiction with experiment. The same results as Miller and Abrahams are obtained if one assumes the correct form of the matrix of the 'chemical shift' potential.

According to the above considerations, the wave function of an electron in the lowest two-center state is of the form [6]

$$u_b(\mathbf{r}) = C_1^- u_\xi(\mathbf{r}) + C_2^- u_\eta(\mathbf{r} - \mathbf{R}), \quad (3.11)$$

and in the higher state

$$u_a(\mathbf{r}) = C_1^+ u_\xi(\mathbf{r}) + C_2^+ u_\eta(\mathbf{r} - \mathbf{R}). \quad (3.12)$$

Here $\mathbf{R}$ is the vector from the first to the second center of the pair. The subscripts ξ and η refer to the positions of the centers in the first or the second sublattices. These subscripts are mutually independent and have the values 1 or 2. We write $u_1(\mathbf{r}) \equiv u(\mathbf{r})$ and $u_2(\mathbf{r}) \equiv \tilde{u}(\mathbf{r})$. If $\xi = \eta$, the vector $\mathbf{R}$ is the primitive translation vector of the lattice. In the opposite case it differs from the primitive translation vector of the lattice by the vector $\pm \mathbf{t}$. The coefficients

of the linear combinations in equations (3.11) and (3.12) were obtained by Miller and Abrahams. They considered only the case of $\xi = \eta$. Here we obtain these coefficients also in the case of $\xi \neq \eta$. They remain real and are of the same form as given by Miller and Abrahams, namely

$$C_1^\pm = z^\pm [1 + (z^\pm)^2 + 2Sz^\pm]^{-1/2}, \quad (3.13)$$

$$C_2^\pm = [1 + (z^\pm)^2 + 2Sz^\pm]^{-1/2}, \quad (3.14)$$

where

$$z^\pm = (\Delta/2W) [1 \pm (1 + 4WS/\Delta + 4W^2/\Delta^2)^{1/2}], \quad (3.15)$$

$$W = W_R - \frac{1}{2}S\Delta + Z, \quad (3.16)$$

$$W_R = L - SJ \quad (3.17)$$

$$L = \langle u_\epsilon(\mathbf{r}) | V_a | u_\eta(\mathbf{r} - \mathbf{R}) \rangle, \quad (3.18)$$

$$J = \langle u_\epsilon(\mathbf{r}) | V_b | u_\epsilon(\mathbf{r}) \rangle, \quad (3.19)$$

$$S = \langle u_\epsilon(\mathbf{r}) | u_\eta(\mathbf{r} - \mathbf{R}) \rangle, \quad (3.20)$$

$$\begin{aligned} Z = & \langle u_\epsilon(\mathbf{r}) | V | u_\eta(\mathbf{r} - \mathbf{R}) \rangle \\ & - \frac{1}{2}S[\langle u_\epsilon(\mathbf{r}) | V | u_\epsilon(\mathbf{r}) \rangle \\ & + \langle u_\eta(\mathbf{r} - \mathbf{R}) | V | u_\eta(\mathbf{r} - \mathbf{R}) \rangle], \end{aligned} \quad (3.21)$$

$$\begin{aligned} \Delta = & \langle u_\epsilon(\mathbf{r}) | V | u_\epsilon(\mathbf{r}) \rangle \\ & - \langle u_\eta(\mathbf{r} - \mathbf{R}) | V | u_\eta(\mathbf{r} - \mathbf{R}) \rangle \geq 0. \end{aligned} \quad (3.22)$$

Here V_a and V_b are the energies of the electron in the Coulombic field of the donor ion a and b , respectively; V is the energy of the electron arising from the external electrostatic potential (we assume this energy to be lower at the center b). The energy difference between the two-center states a and b is

$$\Delta E_{ba} = (1 - S^2)^{-1} (\Delta^2 + 4W^2 + 4WS\Delta)^{1/2}, \quad (3.23)$$

Here we apply the approximation $W = W_R - \frac{1}{2}S\Delta$. It is true if V is approximately linear function of $\mathbf{r}$ in the region of the centers a and b . If $V(\mathbf{r})$ is exactly linear then $Z = 0$ because the orbitals are invariant under the

space inversion. Moreover, we assume $S \ll 1$ what is equivalent to $R \gg a$ and is also the condition justifying the procedure of Miller and Abrahams. Under these assumptions equation (3.23) can be written in the form

$$\Delta E_{ba} = (\Delta^2 + 4W_R^2)^{1/2}. \quad (3.24)$$

Only the quantities Δ , S and W_R are necessary to obtain the coefficients $C_1^\pm$ and $C_2^\pm$ and, also, the energy difference ΔE_{ba} . Here the form of the potential energy V is still not specified. Therefore, we cannot calculate Δ . The quantities S and W_R for Ge and Si in the case of $\xi = \eta$ (both centers in the same sublattice) can be obtained on the basis of equations (3.17–3.20) and (3.1–3.3). Here the factors $\exp(-i\mathbf{p}^{(i)} \cdot \mathbf{R})$ arise in the sum over i because of the performed displacement of the Bloch functions. In the case of Ge each vector $\mathbf{p}^{(i)}$ is a half of the reciprocal lattice vector and, therefore, the exponential factors are equal to $\cos(\mathbf{p}^{(i)} \cdot \mathbf{R})$. In the case of Si the orbitals are the same for both vectors $\mathbf{p}^{(i)}$ and $-\mathbf{p}^{(i)}$. Thus, we can add the two exponential factors which give also the real factor $\cos(\mathbf{p}^{(i)} \cdot \mathbf{R})$. Finally, we obtain [6]

$$\begin{aligned} S_{\text{Ge, Si}} = & \frac{1}{n} \sum_{i=1}^n \exp(-R_i/a) [1 + (R_i/a) \\ & + \frac{1}{2}(R_i/a)^2] \cos(\mathbf{p}^{(i)} \cdot \mathbf{R}), \end{aligned} \quad (3.25)$$

$$\begin{aligned} W_{R\text{Ge, Si}} \approx & -\frac{e^2}{\epsilon R n} \\ & \times \sum_{i=1}^n \exp(-R_i/a) \{ (R/a) [(R_i/a) + 1] \\ & - [1 + (R_i/a) + \frac{1}{2}(R_i/a)^2] \} \cos(\mathbf{p}^{(i)} \cdot \mathbf{R}), \end{aligned} \quad (3.26)$$

where

$$\mathbf{R}_i = [R^2 + (y/(1-y))(\mathbf{R} \cdot \mathbf{k}^{(i)})^2]^{1/2}. \quad (3.27)$$

Here $y = (a^2 - b^2)/a^2$ and ϵ is the static dielectric constant of the crystal. In order to compute the quantities L and J , defined by the formulas (3.18) and (3.19), we replace the

Coulomb potential of the donor ion by the potential having the symmetry of the orbitals. This approximation is justified because the orbitals change much more rapidly than the Coulombic potential. Moreover, we use the approximation

$$\frac{1}{n} \sum_{i=1}^n \frac{1}{R_i} \approx \frac{1}{R}$$

for the function J in equation (3.19). Therefore, equation (3.26) obtained for W_R is also an approximation.

In the case of Ge and $\xi \neq \eta$ (the centers of the pair do not belong to the same sublattice) one has to use also equation (3.9), in addition to equations (3.17–3.20) and (3.1–3.3). Thus we obtain

$$S_{\text{HGe}} = \frac{1}{n} \sum_{i=1}^n \exp(-R_i/a) [1 + (R_i/a) + \frac{1}{2} (R_i/a)^2] \cos(\mathbf{p}^{(i)} \cdot \mathbf{R} \pm \frac{3}{4}\pi), \quad (3.28)$$

$$W_{\text{HGe}} \approx -\frac{e^2}{n\epsilon R} \sum_{i=1}^n \exp(-R_i/a) \times \{ (R/a) [(R_i/a) + 1] - [1 + (R_i/a) + \frac{1}{2} (R_i/a)^2] \} \cos(\mathbf{p}^{(i)} \cdot \mathbf{R} \pm \frac{3}{4}\pi). \quad (3.29)$$

Here the sign '+' refers to the configuration $\xi = 2, \eta = 1$ and the sign '-' to $\xi = 1, \eta = 2$. In both cases the functions $\exp(-i\mathbf{p}^{(i)} \cdot \mathbf{R} \mp \frac{3}{4}\pi)$ arising from the performed transformation of the Bloch functions are real; therefore, the equations (3.28) and (3.29) can be written also in a real form. It should be reminded that the sublattice named 'the first' is transformed to the other sublattice by the nonprimitive translations $\mathbf{r}^{(i)}$ which are parallel (but not anti-parallel) to the vectors $\mathbf{p}^{(i)}$.

In the case of Si and $\xi \neq \eta$ equation (3.10) has to be used instead of equation (3.9). The obtained results are of the same form as (3.25) and (3.26), i.e. $S_{\text{ISI}} = S_{\text{HSI}} = S_{\text{SI}}$ and $W_{\text{RSI}} = W_{\text{HISI}} = W_{\text{RSI}}$. Therefore, in the case of Si equations (3.25) and (3.26) are valid for arbitrary ξ and η .

4. INTERACTION OF ELECTRON WITH THE CRYSTAL LATTICE

(a) The electron-lattice relaxation energy

The energy of the interaction of an electron bound to an isolated donor center with the crystal lattice was calculated in paper 1. There the lowest, singlet state of the electron was considered. Its wave function is of the form (3.1). The energy E_{LR} was obtained as

$$E_{LR} = (4\pi^2 d)^{-1} \int_0^\infty s(\omega) \omega^2 d\omega, \quad (4.1)$$

where

$$s(\omega) = v_L^{-5} \left[\Xi_d^2 U_1 \left(\frac{|\omega|}{v_L} \right) + 2\Xi_d \Xi_u U_2 \left(\frac{|\omega|}{v_L} \right) + \Xi_u^2 U_3 \left(\frac{|\omega|}{v_L} \right) \right] + v_T^{-5} \Xi_u^2 \left[U_4 \left(\frac{|\omega|}{v_T} \right) - U_3 \left(\frac{|\omega|}{v_T} \right) \right] \quad (4.2)$$

$$U_1 \left(\frac{|\omega|}{v_l} \right) = n^{-2} \sum_{i,j=1}^n (4\pi)^{-1} \int D_1^{(i)} \left(\frac{|\omega|}{v_l} \right) \Omega \times D_1^{(j)} \left(\frac{|\omega|}{v_l} \right) d\Omega \quad (4.3)$$

$$U_2 \left(\frac{|\omega|}{v_l} \right) = n^{-2} \sum_{i,j=1}^n (4\pi)^{-1} \times \int (\mathbf{k}^{(i)} \cdot \Omega)^2 D_1^{(i)} \left(\frac{|\omega|}{v_l} \right) \Omega \times D_1^{(j)} \left(\frac{|\omega|}{v_l} \right) d\Omega \quad (4.4)$$

$$U_3 \left(\frac{|\omega|}{v_l} \right) = n^{-2} \sum_{i,j=1}^n (4\pi)^{-1} \times \int (\mathbf{k}^{(i)} \cdot \Omega)^2 (\mathbf{k}^{(j)} \cdot \Omega)^2 \times D_1^{(i)} \left(\frac{|\omega|}{v_l} \right) D_1^{(j)} \left(\frac{|\omega|}{v_l} \right) d\Omega \quad (4.5)$$

$$U_4 \left(\frac{|\omega|}{v_l} \right) = n^{-2} \sum_{i,j=1}^n (4\pi)^{-1} (\mathbf{k}^{(i)} \cdot \mathbf{k}^{(j)}) \times \int (\mathbf{k}^{(i)} \cdot \Omega) (\mathbf{k}^{(j)} \cdot \Omega) D_1^{(i)} \left(\frac{|\omega|}{v_l} \right) \Omega \times D_1^{(j)} \left(\frac{|\omega|}{v_l} \right) d\Omega, \quad (4.6)$$

$$D_1^{(0)}(\mathbf{r}) = \langle F^{(0)}(\mathbf{r}) | \exp(i\mathbf{\tau} \cdot \mathbf{r}) | F^{(0)}(\mathbf{r}) \rangle \\ = (1 + a^2\tau^2/4)^{-2} [1 - z(\mathbf{\Omega} \cdot \mathbf{k}^{(0)})^2]^{-2}, \quad (4.7)$$

with

$$z = y [1 + 4/a^2\tau^2]^{-1}$$

and

$$y = (a^2 - b^2)/a^2.$$

The functions U_1 , U_2 , U_3 and U_4 were given by equations (37–44) for Ge and Si in paper 1. Assuming the same values of the material constants as given in Table 1 Myszkowski and Rogala obtained $E_{LR} = 0.0033$ meV for Ge and $E_{LR} = 0.13$ meV for Si. These figures differ considerably from the values of E_{LR} of Myszkowski and Gómułka [29]. They assumed only one independent deformation potential constant $E_1 = \Xi_a + \frac{1}{3}\Xi_u$ and took into account the interaction of the electron with the acoustic longitudinal phonons only. However, the large difference between the results of these papers is due to different values of the material constants assumed (mainly of the deformation potential constants). Of course, the value of E_{LR} does not depend on whether the center belongs to the first or second sublattice.

Analyzing the integral in the formula (4.1) we found that the main contributions come from the region of $\omega = v_L/a$ in the case of the longitudinal acoustic phonons and of $\omega = v_T/a$ in the case of the transverse phonons. It corresponds to the phonon wave number $\tau = a^{-1}$ for both branches. Such phonons interact, therefore, most strongly with the electron bound to the donor center [21].

(b) The transition probability

In paper 1 the general Gummel–Lax formalism was applied to obtain the transition probability between the two-center donor states of an electron. The wave functions of the initial and final states of the electron were assumed in the form of (3.11) and (3.12), respectively. The considerations were limited to the case of $\xi = \eta$ (both centers in the same sublattice). The assumption of the weak

electron–lattice interaction was not discussed in paper 1 (it is necessary for justification of the Gummel–Lax formalism). This condition for the two-center transitions was given by Blinowski and Mycielski in the form [14]

$$\Delta E_{ba} > 2E_{LR}. \quad (4.8)$$

Using the values of E_{LR} obtained in paper 1 we have $\Delta E_{ba} > 0.007$ meV for Ge and $\Delta E_{ba} > 0.26$ meV for Si.

We consider here only the adiabatic processes for which the frequency of the emitted or absorbed phonon is higher than the frequency of the phonons interacting most strongly with the electron. Using the previous results we obtain the condition

$$\Delta E_{ba} > \frac{\hbar v_L}{a}. \quad (4.9)$$

With the values of the material constants given in Table 1, the resulting conditions are $\Delta E_{ba} > 0.5$ meV for Ge and > 2.7 meV for Si. The condition similar to (4.9) with v_T instead of v_L is weaker because $v_L > v_T$. If the electron–lattice interaction is sufficiently weak, the transition probability formula contains only the terms proportional to the lowest power of the deformation potential constants which play the role of the coupling constants in the perturbation theory. Then both adiabatic and non-adiabatic approximations give the same result. Therefore, in this case we can ignore the condition (4.9) and use our formulas also for the non-adiabatic transitions. The conditions justifying this treatment will be given below.

In paper 1 the transition probability formula was obtained effectively in two particular cases: ‘high frequency’ and ‘low frequency’. In both cases the additional assumptions

$$\Delta^2 \gg 4W_R^2 S^2 \quad (4.10)$$

and

$$4W_R^2 \gg \Delta^2 S^2 \quad (4.11)$$

were introduced to simplify the calculations. These assumptions are satisfied in practical cases.

In the 'high frequency' case the wavelength of the phonon involved in the transition process is smaller than the distance between the centers. The probability of the electron transition from the state a to the state b with emission of one phonon was obtained in the form

$$W_{ba}^{(1)} = \theta \left([\Delta^2 + 4W_R^2]^{1/2} / \hbar \right) [\pi \hbar^3 d]^{-1} \times s([\Delta^2 + 4W_R^2]^{1/2} / \hbar) W_R^2 e^{-\alpha(1-A_\infty)^2}. \quad (4.12)$$

Here the function $s(\omega)$ is given by (4.2) and

$$A_\infty = \frac{g_\infty}{h_\infty} \int_{-\infty}^{+\infty} g(\omega) d\omega \\ \approx \hbar \Delta^2 [2\pi^2 (\Delta^2 + 4W_R^2)^2 d]^{-1} \times \int_0^\infty \text{cth}(\hbar\omega/2kT) s(\omega) \omega^3 d\omega \quad (4.13)$$

$$\alpha = \int_{-\infty}^{+\infty} f(\omega) d\omega \approx \Delta^2 [2\pi^2 \hbar (\Delta^2 + 4W_R^2) d]^{-1} \times \int_0^\infty \text{cth}(\hbar\omega/2kT) s(\omega) \omega d\omega. \quad (4.14)$$

The integrands f , g and h in equations (4.13) and (4.14) are approximated by f_∞ , g_∞ and h_∞ , respectively, what is an additional approximation independent from the previous 'high frequency' assumption. It is justified, if the main contributions to the integrals come from the region of ω which fulfills the 'high frequency' assumption. It is true for almost all values of R in the case of equation (4.13), but only for $R > 9a$ in the case of equation (4.14). Moreover, the function $\text{cth}(\hbar\omega/2kT)$ under the integrals (4.13) and (4.14) is replaced by 1, which is its value at $T = 0$. However, this approximation can be used with a good accuracy also for $T < \sqrt{\frac{3}{5}}(\hbar v_L/ka)$ in equation (4.13) and for $T < \sqrt{\frac{1}{5}}(\hbar v_L/ka)$ in equation (4.14). Finally, the approximate formulas are

$$A_\infty \approx C \Delta^2 (\Delta^2 + 4W_R^2)^{-2}, \quad (4.15)$$

$$\alpha \approx B \Delta^2 (\Delta^2 + 4W_R^2)^{-1}. \quad (4.16)$$

The constants C and B were obtained also in paper 1 (see Table 2). It can be shown that the value of B is very low in both materials also if $R < 9a$. On the other hand, the minimum value of the coefficient $\exp(-\alpha)$ in the transition probability formula is $\exp(-B)$. Therefore, this coefficient can be neglected and the simplified transition probability formula can be used for all relevant values of R . Now we have to assume only the weaker condition on the temperature, i.e.

$$T < \sqrt{\frac{3}{5}} \frac{\hbar v_L}{ka}$$

which justifies equation (4.15). With the values of the material constants given in Table 1 the resulting conditions are $T < 4.5^\circ\text{K}$ for Ge and $T < 24.6^\circ\text{K}$ for Si.

The inequality $\alpha \ll 1$ is valid for both materials; therefore, we can limit our considerations to the one-phonon processes only. Multi-phonon processes are much less probable and can be neglected [19-21].

Moreover, if the inequality $A_\infty \ll 1$ is valid, there are only terms proportional to the deformation potential constants squared in equation (4.12). These terms are involved in the function $s(\omega)$. In this case we can ignore the condition (4.9) and use equation (4.12) in more wide range of the transition energies.

In the 'low frequency' case the wavelength of the involved phonon is larger than the distance between the centers. The probability of the transition from the state a to the state b , with simultaneous emission of one phonon was obtained as

$$W_{ba}^{(1)} \approx W_{ba0}^{(1)} + W_{ba2}^{(1)}, \quad (4.17)$$

where

$$W_{ba0}^{(1)} = [540\pi \hbar^3 d]^{-1} (2v_L^{-5} + 3v_T^{-5}) \Xi_u^2 X_1 \Delta^2 \\ \times \theta([\Delta^2 + 4W_R^2]^{1/2} / \hbar) \\ \times \exp(-\alpha)(1-A_0)^2, \quad (4.18)$$

$$W_{ba2}^{(1)} = [6\pi\hbar^5 v_L^7 d]^{-1} E_1^2 R^2 W_R^2 (\Delta^2 + 4W_R^2) \times \theta[(\Delta^2 + 4W_R^2)^{1/2}/\hbar] \times \exp(-\alpha)(1-A_2)^2. \quad (4.19)$$

Here

$$X_{\text{IGe,Sl}} = \sum_{i=1}^n \cos^2(\mathbf{p}^{(i)} \cdot \mathbf{R}) \times \langle (F^{(i)}(\mathbf{r}) | F^{(i)}(\mathbf{r}-\mathbf{R})) \rangle^2 - n S_{\text{IGe,Sl}}^2 \quad (4.20)$$

$$\alpha = \int_{-\infty}^{+\infty} f(\omega) d\omega, \quad (4.21)$$

$$A_0 = \frac{g_0}{h_0} \int_{-\infty}^{+\infty} g(\omega) d\omega, \quad (4.22)$$

$$A_2 = \frac{g_2}{h_2} \int_{-\infty}^{+\infty} g(\omega) d\omega. \quad (4.23)$$

To obtain the formula (4.19) Myszkowski and Rogala used the assumptions (4.10) and (4.11). Then, the integrals in equations (4.21-4.23) were approximated similarly as in the 'high frequency' case. The obtained results are $A_0 = -4(W_R^2/\Delta^2)A_\infty$ and $A_2 = A_\infty$. Moreover, the quantity α was obtained in the same form as previously in the 'high frequency' case.

In the 'low frequency' case, as a rule, the adiabatic assumption cannot hold. The energy of the phonon involved in the transition process must be lower than the energy of the phonons interacting most strongly with the electron. Nevertheless, the formula (4.17) can be used for nonadiabatic transition processes, if $A_0 \ll 1$ and $A_2 \ll 1$. In that case the transition probability formula involves only the terms proportional to the deformation potential constants squared [21]. However, the last condition together with the 'low frequency' assumption can be satisfied only in a very narrow range of ΔE_{ba} .

The problem of the non-adiabatic processes was examined by Takeyama [21], who took into account only diagonal matrix elements of the perturbing phonon operator between the one-center wave functions (in the 'site' representation. However, expanding the

functions f , g and h in powers of τ , it was shown in paper 1 that also nondiagonal matrix elements are important. Both in the 'high frequency' and 'low frequency' cases the transition probability of the reverse process (the transition from the state b to the state a with simultaneous absorption of a phonon) can be obtained easily, replacing the function $\theta(\omega)$ by $\theta(-\omega)$ in equation (4.12) or in equations (4.18) and (4.19).

All the results of paper 1 both in the 'high frequency' and 'low frequency' cases can be obtained also if the centers of the pair do not belong to the same sublattice. In the case of Ge and $\xi \neq \eta$ the two-center wave functions (3.11) and (3.12) can be represented in the general forms (2.5) and (2.6) with the help of equations (3.1) and (3.9) if one assumes

$$F_b^{(i)}(\mathbf{r}) = C_1^- F^{(i)}(\mathbf{r}) + C_2^- F^{(i)}(\mathbf{r}-\mathbf{R}) \times \exp(-i\mathbf{p}^{(i)} \cdot \mathbf{R} \mp \frac{1}{2}i\pi)$$

and

$$F_a^{(i)}(\mathbf{r}) = C_1^+ F^{(i)}(\mathbf{r}) + C_2^+ F^{(i)}(\mathbf{r}-\mathbf{R}) \times \exp(-i\mathbf{p}^{(i)} \cdot \mathbf{R} \mp \frac{1}{2}i\pi).$$

Here the upper and the lower sign in the function $\exp(-i\mathbf{p}^{(i)} \cdot \mathbf{R} \mp \frac{1}{2}i\pi)$ correspond to the cases $\xi=2, \eta=1$ and $\xi=1, \eta=2$, respectively (see Section 3). Using the last two formulas in equations (2.7-2.9) we obtain the appropriate phonon distribution functions. They differ from the functions (67-69) of paper 1 because the quantities $\cos(\mathbf{p}^{(i)} \cdot \mathbf{R})$, S and W_R are replaced by $\cos(\mathbf{p}^{(i)} \cdot \mathbf{R} \pm \frac{1}{2}\pi)$, S_{IIIGe} and W_{RIIGe} , respectively (see equations (3.28) and (3.29)). Under the same assumptions as previously the resulting formulas for the hopping probability are similar to (4.12) or (4.17-4.19). The only difference is that the quantity W_{R1} is replaced by W_{RIIGe} and X_1 (defined by (4.20)) by

$$X_{\text{IIIGe}} = \sum_{i=1}^n \cos^2(\mathbf{P}^{(i)} \cdot \mathbf{R} \pm \frac{1}{2}\pi) \times \langle (F^{(i)}(\mathbf{r}) | F^{(i)}(\mathbf{r}-\mathbf{R})) \rangle^2 - n S_{\text{IIIGe}}^2. \quad (4.24)$$

In the case of Si and $\xi \neq \eta$ the one-center wave function is used in both forms (3.1) and (3.10) (instead of (3.9) in the case of Ge) in equations (3.11) and (3.12). Comparison with equations (2.5) and (2.6) gives

$$F_b^{(0)}(\mathbf{r}) = C_1^{-1} F^{(0)}(\mathbf{r}) + C_2^{-1} F^{(0)}(\mathbf{r} - \mathbf{R}) \\ \times \exp(-i\mathbf{p}^{(0)} \cdot \mathbf{R})$$

and

$$F_a^{(0)}(\mathbf{r}) = C_1^{-1} F^{(0)}(\mathbf{r}) + C_2^{-1} F^{(0)}(\mathbf{r} - \mathbf{R}) \\ \times \exp(-i\mathbf{p}^{(0)} \cdot \mathbf{R}).$$

Using these formulas in equations (2.7–2.9) we obtain the phonon distribution functions in the same form as given by equations (67–69) of paper 1. It should be reminded here that the quantities S_{ISI} and W_{RISI} are of the same form as S_{IISI} and W_{RIISI} , respectively. Therefore, the resulting hopping probability formulas are of the same form as (4.12) or (4.17–4.19) (see also paper 1).

The transition probability is a rapidly oscillating function of $\mathbf{R}$ because W_{RI} and X_{I} (or W_{RII} and X_{II}) involve the functions $\cos(\mathbf{p}^{(0)} \cdot \mathbf{R})$ (or $\cos(\mathbf{p}^{(0)} \cdot \mathbf{R} \pm \frac{1}{2}\pi)$). However, this oscillating part is unimportant in the theories of the macroscopic phenomena in the crystal, e.g. hopping conductivity [1–13]. These phenomena involve a large number of donor pairs distributed statistically in the crystal. Therefore, the averaged transition probability can be used which does not oscillate rapidly, but has only the main, slow dependence on $\mathbf{R}$. It is very difficult to average directly the transition probability; therefore, we use an approximation replacing W_{RI} and X_{I} by their ‘averages’ $\overline{W_{\text{RI}}}$ and $\overline{X_{\text{I}}}$ (and, respectively, W_{RII} and X_{II} by $\overline{W_{\text{RII}}}$ and $\overline{X_{\text{II}}}$) in equations (4.12–4.14) and (4.18–4.19). Using also the previous approximation we obtain in the ‘high frequency’ case

$$\tilde{W}_{ba0}^{(1)} = \theta([\Delta^2 + 4\overline{W_R^2}]^{1/2}/\hbar) [\pi\hbar^3 d]^{-1} \\ \times s([\Delta^2 + 4\overline{W_R^2}]^{1/2}/\hbar) \overline{W_R^2}$$

$$\times [1 - C\Delta^2(\Delta^2 + 4\overline{W_R^2})^{-2}]^2, \quad (4.25)$$

and in the ‘low frequency’ case

$$\tilde{W}_{ba}^{(1)} = \tilde{W}_{ba0}^{(1)} + \tilde{W}_{ba2}^{(1)}, \quad (4.26)$$

where

$$\tilde{W}_{ba0}^{(1)} = [540\pi\hbar^3 d]^{-1} \theta([\Delta^2 + 4\overline{W_R^2}]^{1/2}/\hbar) \\ \times (2v_L^{-5} + 3v_T^{-5}) \Xi_u^2 \Delta^2 \overline{X} \\ \times [1 + 4C\overline{W_R^2}(\Delta^2 + 4\overline{W_R^2})^{-2}]^2, \quad (4.27)$$

$$\tilde{W}_{ba2}^{(1)} = [6\pi\hbar^5 v_L^7 d]^{-1} \theta([\Delta^2 + 4\overline{W_R^2}]^{1/2}/\hbar) \\ \times E_1^2 R^2 \overline{W_R^2} (\Delta^2 + 4\overline{W_R^2}) \\ \times [1 - C\Delta^2(\Delta^2 + 4\overline{W_R^2})^{-2}]^2. \quad (4.28)$$

Here the factor $\exp(-\alpha)$ is neglected. The assumptions (4.10) and (4.11) can also be written in the ‘averaged’ form

$$\Delta^2 \gg 4\overline{W_R^2} S^2, \quad (4.29)$$

and

$$4\overline{W_R^2} \gg \Delta^2 S^2. \quad (4.30)$$

In the following we will obtain the quantities $\overline{S^2}$, $\overline{X}$ and $\overline{W_R^2}$ and we will point out that $\overline{S_{\text{I}}^2} = \overline{S_{\text{II}}^2}$, $\overline{X_{\text{I}}} = \overline{X_{\text{II}}}$ and $\overline{W_{\text{RI}}^2} = \overline{W_{\text{RII}}^2}$ in both materials. Therefore, relations (4.25–4.30) can be used for arbitrary ξ and η .

Using equation (3.26) for $\xi = \eta$ in the case of Ge and for arbitrary ξ and η in the case of Si we can write

$$W_{\text{RI(Ge, Si)}}^2 = \sum_{i,j=1}^n A_{ij}(\mathbf{R}) \cos(\mathbf{p}^{(i)} \cdot \mathbf{R}) \\ \times \cos(\mathbf{p}^{(j)} \cdot \mathbf{R}). \quad (4.31)$$

Using equation (3.29) in the case of Ge and $\xi \neq \eta$ we obtain

$$W_{\text{RII(Ge)}}^2 = \sum_{i,j=1}^n A_{ij}(\mathbf{R}) \cos(\mathbf{p}^{(i)} \cdot \mathbf{R} \pm \frac{1}{2}\pi) \\ \times \cos(\mathbf{p}^{(j)} \cdot \mathbf{R} \pm \frac{1}{2}\pi). \quad (4.32)$$

The functions $A_{ij}(\mathbf{R})$ in equations (4.31) and

(4.32) are slowly-varying functions in the relevant range of R . The products of the functions $\cos(\mathbf{p}^{(i)} \cdot \mathbf{R})$ and $\cos(\mathbf{p}^{(i)} \cdot \mathbf{R} \pm \frac{1}{2}\pi)$ can be written in another form, namely

$$W_{\text{Ge,S}}^2 = \frac{1}{2} \sum_{i,j=1}^n A_{ij}(\mathbf{R}) [\cos((\mathbf{p}^{(i)} + \mathbf{p}^{(j)}) \cdot \mathbf{R}) + \cos((\mathbf{p}^{(i)} - \mathbf{p}^{(j)}) \cdot \mathbf{R})], \quad (4.33)$$

$$W_{\text{HGe}}^2 = \frac{1}{2} \sum_{i,j=1}^n A_{ij}(\mathbf{R}) \times [\cos((\mathbf{p}^{(i)} + \mathbf{p}^{(j)}) \cdot \mathbf{R} \pm \frac{1}{2}\pi) + \cos((\mathbf{p}^{(i)} - \mathbf{p}^{(j)}) \cdot \mathbf{R})]. \quad (4.34)$$

Consider the case of Ge and $\xi = \eta$. Each vector is a half of a reciprocal lattice vector. The vector $\mathbf{p}^{(i)} + \mathbf{p}^{(j)}$ in equation (4.33) are the reciprocal lattice vectors only if $i = j$. The vectors $\mathbf{p}^{(i)} - \mathbf{p}^{(j)}$ are equal to zero for $i = j$, but for $i \neq j$ are not the reciprocal lattice vectors. The vector $\mathbf{R}$ is an arbitrary vector of a primitive translation of the lattice. Therefore, the function $\cos((\mathbf{p}^{(i)} + \mathbf{p}^{(j)}) \cdot \mathbf{R}) + \cos((\mathbf{p}^{(i)} - \mathbf{p}^{(j)}) \cdot \mathbf{R})$ in equation (4.33) is equal 2 in the case of $i = j$ for arbitrary $\mathbf{R}$, but in the case of $i \neq j$ its value depends on $\mathbf{R}$ and it runs over the numbers $-2, 0, +2$. The same properties has the function

$$\cos((\mathbf{p}^{(i)} + \mathbf{p}^{(j)}) \cdot \mathbf{R} \pm \frac{1}{2}\pi) + \cos((\mathbf{p}^{(i)} - \mathbf{p}^{(j)}) \cdot \mathbf{R})$$

in equation (4.34) for Ge and $\xi \neq \eta$. The functions $A_{ij}(\mathbf{R})$ are slowly-varying compared with the trigonometric functions; therefore, we can average equations (4.33) and (4.34) over some volume $K(\mathbf{R})$ (the sphere, for instance). This volume has its center at the point $\mathbf{R}$ and is large compared with the volume of the unit cell but sufficiently small to consider the orbitals as approximately constant inside it.

In the integration the terms with $i = j$ have to be kept in the sum, but those with $i \neq j$ vanish (they change their value and sign many

times in the integration volume). Thus, using (4.33) we obtain

$$\begin{aligned} \overline{W_{\text{HGe}}^2} &= \frac{1}{|V|} \int_V W_{\text{HGe}}^2 d\mathbf{v} = \frac{1}{|V|} \int_V \frac{1}{2} \sum_{i,j=1}^n A_{ij}(\mathbf{R}) \\ &\times [\cos((\mathbf{p}^{(i)} + \mathbf{p}^{(j)}) \cdot \mathbf{R}) + \cos((\mathbf{p}^{(i)} - \mathbf{p}^{(j)}) \cdot \mathbf{R})] \\ &= \frac{1}{|V|} \cdot \frac{1}{2} \sum_{i,j=1}^n A_{ij}(\mathbf{R}) \cdot 2|V|\delta_{ij} \\ &= \sum_{i=1}^n A_{ii}(\mathbf{R}). \end{aligned} \quad (4.35)$$

Performing the average in equation (4.34) separately for the two configurations $\xi = 1$, $\eta = 2$ and $\xi = 2$, $\eta = 1$ we obtain the same results. Thus, in the case of Ge, for arbitrary ξ and η , the averaged value of the square of the 'resonance energy' $\overline{W_{\text{HGe}}^2}$ is of the same form. Comparing equations (3.26), (4.31) and (4.35) yields

$$\begin{aligned} \overline{W_{\text{HGe}}^2} &= \left(\frac{e^2}{n\epsilon R} \right)^2 \sum_{i=1}^n \exp(-2R_i/a) \\ &\times \{ (R/a) [(R_i/a) + 1] \\ &- [1 + (R_i/a) + \frac{1}{2}(R_i/a)^2] \}^2. \end{aligned} \quad (4.36)$$

In the case of Si the vectors $\mathbf{p}^{(i)}$ are not whole multiple of a half of a reciprocal lattice vector. Therefore, the functions $\cos((\mathbf{p}^{(i)} - \mathbf{p}^{(j)}) \cdot \mathbf{R})$ and $\cos((\mathbf{p}^{(i)} + \mathbf{p}^{(j)}) \cdot \mathbf{R})$ in equation (4.33) are equal 1 for all $\mathbf{R}$ only if $\mathbf{p}^{(i)} = \mathbf{p}^{(j)}$ or $\mathbf{p}^{(i)} = -\mathbf{p}^{(j)}$ and, in other cases, depend on $\mathbf{R}$ and run over the range from -1 to $+1$. The resulting average is of the same form as (4.36) (the formula for $|W|^2$ given by Miller and Abrahams is also of the same form).

The quantities S_i^2 and X_i can be represented in a similar way as it was done for W_{H}^2 (in equation (4.31)), and also the quantities S_{H}^2 and X_{H} —as W_{H}^2 (in equation (4.32)). Then, performing the average in the same manner as for W_{RI} and W_{RII} , we obtain on the basis of

equations (3.25) and (3.28) for Ge and Si

$$\begin{aligned} \overline{S}_f^2 = \overline{S}_h^2 = \overline{S}^2 &= \frac{1}{n^2} \sum_{i=1}^n \exp(-2R_i/a) \\ &\times [1 + (R_i/a) + \frac{1}{2}(R_i/a)^2]^2, \end{aligned} \quad (4.37)$$

and, on the basis of equations (4.20) and (4.24)

$$\overline{X}_I = \overline{X}_{II} = n(n-1)\overline{S}^2. \quad (4.38)$$

5. DISCUSSION OF RESULTS

In this paper we consider the probability of the phonon-induced hopping transitions in n -type Ge and Si. We use the general results of paper 1 for the phonon distribution functions and the transition probability [18]. We consider the system of two donor centers and one electron in an external, static electric field. We are interested in the probability of the electron transitions between the two lowest states. Only the transitions involving one phonon are taken into account. The results of paper 1 for the two-center transitions are generalized to the case of the impurity centers in arbitrary substitutional sites, i.e. not only in the same sublattice. The transition probability depends on the difference of the electrostatic energy between the centers, the resonance energy and some other overlap integrals. If the centers do not belong to the same sublattice, the obtained formula for the transition probability is of the same form as given in paper 1. However, the resonance energy and the overlap integrals themselves depend in a different way on the distance between the centers.

The general assumptions of the weak electron-phonon interaction and of the adiabatic character of the process [17] should be satisfied, in particular, for the two-center transitions. We obtain the appropriate conditions on the energy difference between the states resulting from these assumptions. However, the adiabatic condition cannot be fulfilled in the 'low frequency' case, what was not pointed out in paper 1. Nevertheless, the

obtained formula can be used if it contains the deformation potential constants only in the lowest power. In this case the adiabatic condition can be ignored, however the range of applicability of the formula becomes very small. On the other hand, both conditions can be easily satisfied in the 'high frequency' case. Moreover, we discuss the zero-temperature assumption used in paper 1 and give the upper limit for the temperature of the crystal. This condition is well met in the region of the hopping phenomena.

To eliminate the oscillating component of the transition probability we perform the average over small regions around each of the centers. The resulting formulas are slowly-varying functions of the vector $\mathbf{R}$ connecting the centers. They are convenient in practical cases, i.e. in calculations of the macroscopic phenomena [1-14].

In order to extend the transition probability theory we obtain the two-center wave functions in the case of the donor centers at arbitrary substitutional sites. To do this, we perform the transformation of the one-center wave function connected with the displacement of the donor center from one crystal sublattice to the other. Then this result is used to generalize the Miller-Abrahams [6] procedure. The obtained two-center wave functions are of the same form as given by Miller and Abrahams, i.e. they are linear combinations of the one-center wave functions. However, the coefficients in these combinations involve the resonance energy and the overlap integral which, in the case of Ge, depend on the arrangement of the centers.

The results of our paper can be used in the theories of the macroscopic phenomena induced by the hopping transitions [1-14]. The substantial limitation of the theory is the adiabatic condition which gives the lower limit of the phonon energy. It seems that the nonadiabatic processes play a significant role at very low temperatures of the crystal. Therefore, the presented theory of the two-center

transitions needs an extension to the non-adiabatic case, which was started by Takeyama[21].

Acknowledgements—The author wishes to express his gratitude to Dr. J. Mycielski and to Professor M. Suffczynski for many valuable discussions and remarks.

REFERENCES

1. CONWELL E. M., *Phys. Rev.* **103**, 51 (1956).
2. MOTT N. F., *Can. J. Phys.* **34**, 1356 (1956).
3. KASUA T. and KOIDE S., *J. phys. Soc. Japan* **13**, 1287 (1958).
4. MOTT N. F. and TWOSE W. D., *Adv. Phys.* **10**, 107 (1961).
5. CSAVINSZKY P., *Phys. Rev.* **119**, 1605 (1960).
6. MILLER A. and ABRAHAMS E., *Phys. Rev.* **120**, 745 (1960).
7. POLLAK M. and GEBALLE T. H., *Phys. Rev.* **122**, 1742 (1961).
8. SLADEK R. J. and KEYES R. W., *Phys. Rev.* **122**, 437 (1961).
9. YAMANOUCI C., *J. phys. Soc. Japan* **18**, 1775 (1963).
10. POLLAK M., *Phys. Rev.* **133**, A564 (1964).
11. TANAKA S., KOBAYASHI M., HANAMURA E. and UCHINOKURA K., *Phys. Rev.* **134**, A256 (1964).
12. GOLIN S., *Phys. Rev.* **132**, 178 (1963).
13. POLLAK M. and WATT D. H., *Phys. Rev.* **140**, A87 (1965).
14. BLINOWSKI J. and MYCIELSKI J., *Phys. Rev.* **136**, A266 (1964); **140**, A1024 (1965).
15. MILWARD R. C. and NEURINGER L. J., *Phys. Rev. Lett.* **15**, 664 (1965).
16. MILWARD R. C. and AGGARWAL L., *J. phys. Soc. Japan Suppl.* **21**, 582 (1966).
17. GUMMEL H. and LAX M., *Ann. Phys.* **2**, 28 (1957).
18. MYSZKOWSKI A. and ROGALA M., *Phys. Rev.* **168**, 768 (1968).
19. MYCIELSKI J., *Phys. Rev.* **125**, 46 (1962).
20. KANE E. O., *Phys. Rev.* **119**, 40 (1960).
21. TAKEYAMA K., *J. phys. Soc. Japan* **23**, 1013 (1967).
22. KOHN W., *Solid-State Physics* (Edited by F. Seitz and D. Turnbull), Vol. 5, p. 257. Academic Press, New York (1957).
23. MYSZKOWSKI A., to be published in *Phys. Rev.*
24. TAKEYAMA K., KAWAHITO M., OKAZAKI M. and KIKUCHI M., *J. phys. Soc. Japan* **22**, 118 (1967).
25. AGGARWAL R. L., *Solid State Commun.* **2**, 163 (1964).
26. REUSZER J. H. and FISHER P., *Phys. Rev.* **135**, A1125 (1964).
27. REUSZER J. H. and FISHER P., *Bull. Am. phys. Soc.* **9**, 645 (1964).
28. AGGARWAL R. L. and RAMDAS A. K., *Phys. Rev.* **137**, A602 (1965).
29. MYSZKOWSKI A. and GÓMULKAS., *Phys. Rev.* **134**, A1102 (1964).

CHARACTERIZATION OF RbOH-GROWN QUARTZ BY INFRARED AND MASS SPECTROSCOPY*

O. C. KOPP

Metals and Ceramics Division

and

P. A. STAATS

Physics Division, Oak Ridge National Laboratory, Oak Ridge, Tenn. 37830, U.S.A.

(Received 24 October 1969; in revised form 22 December 1969)

Abstract—Infrared frequencies of RbOH-grown quartz include bands at 3200, 3300, 3350, 3396, 3438, 3475, 3500, 3515, 3555 and 3580 cm^{-1} in the region 3200 to 3600 cm^{-1} . An unusual time- (or temperature-) related phenomenon causes an increase in absorbance in the region 2900 to 3550 cm^{-1} when crystals are examined over intervals up to several hours while held in a liquid nitrogen cell. The band at 3580 cm^{-1} is not affected. A linear relationship exists between average growth rate and extinction coefficient (α_{3580}/cm) which is influenced by the temperature of the growth zone. Typically, the extinction coefficient decreases (and presumably the crystal quality improves) as the growth temperature increases for a given growth rate. Impurity ions such as Li^+ , Na^+ and K^+ present in the RbOH solvent are taken preferentially into the quartz structure because of their smaller sizes. Aluminium and iron present are derived from the nutrient and vessel liner, respectively. The ratio of Fe^{+3} and Al^{+3} to total alkalis is close to but slightly greater than one.

1. INTRODUCTION

CONSIDERABLE effort has been made to perfect the growth of high-quality quartz which is essential to many piezoelectric devices. Some studies[1] have related the internal friction (anelastic loss) for synthetic quartz to its growth rate. More recently, Dodd and Fraser [2] have shown a relationship between the anelastic loss and the infrared extinction coefficient at 3500 cm^{-1} . Crystals of good quality have low anelastic losses and low extinction coefficients. Dodd and Fraser[2] state that since there is a correlation between α_{3500} of the broad background absorption due to bonded OH and the 5 mc anelastic loss at the peak near 100°C , it is very probable that this peak is due to hydrogen bonded OH. Shifts in the spectral patterns of quartz grown from D_2O [3,4] appear to confirm the important role of OH bonding on the infrared absorption bands in the region from 3000 to

4000 cm^{-1} . The piezoelectric quality of quartz has been improved by adding impurities to the growth solution[5,6].

Most synthetic quartz has been grown in solutions of NaOH or Na_2CO_3 with or without dopants. Only recently has any attention been given to the growth of quartz from solvents of the less common alkalies[7]. The purpose of this paper is to report further on the growth of quartz using RbOH solvent and to present the results of infrared studies on these crystals. A relationship is shown to exist between growth rate and infrared extinction coefficients at 3580 and 3500 cm^{-1} which appears to be influenced primarily by the temperature of the growth zone. We agree with the basic conclusion[2-4] that the infrared absorption bands in the region 3000 to 4000 cm^{-1} for α -quartz are due to OH. However, the results of the present study do not permit us to assign specific peaks to any definite OH configurations or associations.

*Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

†Consultant from the Department of Geology, University of Tennessee, Knoxville.

2. SYNTHESIS AND CHARACTERIZATION OF RbOH-GROWN QUARTZ

A description of the typical procedures used

for growing quartz hydrothermally is given by Laudise[8]. Further details concerning the growth of quartz using RbOH are given by Kopp and Clark[7]. In all cases 0.5 *N* RbOH was used as a solvent and the autoclaves contained low-carbon steel liners. Since that report was prepared, a large number of crystals have been grown for infrared study. A summary of the growth conditions for all the crystals used in this study is presented in Table 1. The seeds used were AT-cut oscillator plates.

A crystal from experiment number 170 was analyzed using a spark source mass spectrometer (except for Fe which was analyzed by emission spectroscopy). The results are reported in Table 2.

While additional analyses would be desirable, several factors make reliable analyses of quartz difficult to obtain. Foremost among these is the fact that the concentrations of impurities are not uniform throughout its volume. Variations may be observed outward from the seed[9] and also along specific growth directions[10]. Examination of analytical data presented by Laudise, Ballman, and King[11] suggests that a crystal analyzed by the same method in different laboratories (or by different techniques) may give considerably different results. For example, the iron concentration of a crystal grown in 1.0 *M* NaOH was reported to be 97 and 50 ppm SiO₂ by independent spectrochemical analyses and 870 ppm SiO₂ by activation analysis.

Perhaps more significant than the actual values reported in Table 2 are some relationships among the values. The RbOH-grown crystal contains traces of Li, Na and K, while Cs is very low. Analysis of the 0.5 *N* RbOH solvent used for growth reveals the presence of 0.5 µg/ml, Li; 53 µg/ml, Na; 680 µg/ml, K; and 450 µg/ml, Cs (by flame photometry considered to be accurate to ± 5 per cent of reported values). The smaller Li⁺ and Na⁺ ions, and even the relatively large K⁺ ion (which has the same size as the OH⁻ ion) may be incorporated more readily into the structure than larger ions such as Rb⁺ or Cs⁺. Kats [3] was able to electrodiffuse plus one ions up to potassium in size into quartz crystals, but failed to incorporate the larger Rb⁺ or Tl⁺ ions in this structure.

Another interesting relationship is that the

ratio of total Fe⁺³ and Al⁺³ to the total plus one ions is close to (but slightly greater than) one* for both the nutrient and RbOH-grown crystal. This suggests that electrical neutrality within the crystal structure is being maintained by the following mechanism: each time a plus three ion substitutes for a silicon ion in the lattice a plus one ion is also incorporated.

Kats[3] observed that the total amount of alkali impurity was equal to the sum of Al⁺³ and Fe⁺³ in synthetic quartz. Cohen and Hodge [10] observed that the concentrations of lithium and sodium followed the same order of concentration as aluminum in the various zones of synthetic quartz crystals. The relationship between plus one and plus three ions raises an interesting question concerning the role and position of (OH)⁻ [2, 3, 4] ions in the quartz structure. Hydroxyl ions might be located on oxygen sites (of tetrahedra where Al⁺³ or Fe⁺³ has substituted for a Si⁺⁴ ion), in which event a link in the three dimensional framework would be broken, or they might reside in the open space of the crystal lattice in the vicinity of plus one ion impurities. Unfortunately, the chemical analyses and the interpretation of the infrared data are not precise enough at this time to determine the extent to which each mode operates.

Based on the chemical analyses, we believe that the aluminum present in the RbOH-grown crystal was inherited from the nutrient. The iron was added to the system by the corrosion of the low-carbon steel liner of the hydrothermal vessel. The development of rubidium iron silicates[7] on the walls and internal parts of the vessel kept corrosion from becoming excessive.

3. INFRARED STUDIES OF RbOH-GROWN QUARTZ

While the infrared spectrum (at liquid nitrogen temperature) of RbOH-grown quartz is generally similar to that of natural or synthetic quartz grown from other alkaline solvents,

*Ratios ranging from 1.2 to 1.9 were obtained for several crystals grown in various alkali hydroxide solvents.

Table 1. Summary of growth conditions and extinction coefficient determinations for RbOH-grown quartz crystals*

Crystal number	Growth temp.	Base temp.	Pressure	Duration	Thickness (i.r. beam)	Average growth rate (i.r. beam)	Extinction coefficient at 3580 cm ⁻¹	Extinction coefficient at 3500 cm ⁻¹	Remarks
88M	396	414	1.3	35	7.3	0.21	1.42	1.23	
94U	384	402	1.2	63	6.2	0.10	0.29	0.18	
163U	374	406	1.7	21	4.0	0.19	0.89	1.19	⊥ prism
165U	382	424	0.9	49	3.3	0.07	0.33	0.17	⊥ prism
170U	460	490	1.2	27	7.3	0.27	0.22	0.11	⊥ prism
172U	356	400	0.8	28	3.5	0.13	0.45	0.26	
194U	311	344	0.9	14	1.0	0.07	1.11	1.21	
196U	390	420	1.6	14	5.0	0.36	1.06	0.56	
197U	456	484	1.5	13	7.3	0.56	0.42	0.25	⊥ prism
200U	438	460	1.8	17	4.8	0.28	0.72	0.33	
200M	438	460	1.8	17	4.2	0.25	0.74	0.32	
207U	450	486	1.2	7	3.8	0.54	0.70	0.29	
207M	450	486	1.2	7	3.9	0.56	0.62	0.20	
208U	449	484	1.2	14	6.5	0.46	0.52	0.18	
211U	449	486	1.2	20	7.1	0.35	0.46	0.15	
211M	449	486	1.2	20	6.4	0.32	0.34	0.12	⊥ prism
213U	445	484	1.2	22	7.7	0.35	0.34	0.08	
216U	458	487	1.2	28	7.6	0.27	0.46	0.20	⊥ prism
216M	458	487	1.2	28	7.5	0.27	0.35	0.15	⊥ prism
219U	414	438	0.8	21	6.2	0.30	0.32	0.11	⊥ prism
219M	414	438	0.8	21	4.1	0.20	0.27	0.17	
							0.46	0.10	

* U and M refer to upper and middle seeds, respectively; temperatures, °C ± 5°C; pressures, Kb ± 0.1 Kb; duration, days; thicknesses, mm parallel to direction of transmission of beam; growth rates, mm/day; extinction coefficient = α/cm = absorbance ÷ effective sample thickness (cm) at specified frequencies; remarks, beam normal to minor rhombohedron unless otherwise stated.

Table 2. Chemical analyses of nutrient and RbOH-grown quartz (ppm SiO₂)*

	Al	Cs	Fe	K	Li	Na	Rb	Total alkalies	Total Fe + Al	Ratio +3/+1 ions
Nutrient	70	<1	<3	10	<20	10	<1	<42	<73	~1.7
RbOH-grown (No. 170M)	70	<1	50	30	20	10	40	<101	~120	~1.2

*Spark source mass spectrometer, sample size 300–500 mg, bismuth carrier (except Fe which was done by emission spectroscopy). Values fall in the range $\frac{1}{2}x-2x$ (e.g. for Na = 10 ppm, several analyses of the same sample would normally fall in the range 5–20 ppm) and are believed to be accurate within the limits of precision.

Table 3. Infrared frequencies of RbOH-grown quartz in the region 3200 cm⁻¹–3600 cm⁻¹ at ~77°K

Frequencies (cm ⁻¹)	Intensities	Notes
3200	Medium; broad	Overtone or combination band of Si–O vibrations. These bands are found in both natural and synthetic quartz and are not affected by growth method, ion impurities, etc. Characteristic of RbOH- and KOH-grown quartz. This band appears in nearly all synthetic quartz spectra. With the exception of CsOH-grown crystals, the intensity of this band increases with ionic size from Na ⁺ to Rb ⁺ .
3300	Medium; broad	
3350	Medium	
3368	Weak	Band from natural seed plate. This band is one of the strongest absorption bands of natural quartz in this region. We have observed it from our seed plates alone and have removed it from the spectra of RbOH-grown quartz by slicing the crystal at the seed plane.
3396	Strong	Characteristic of synthetic quartz. These bands are found in all synthetic quartz crystals. They seem to follow the same intensity relationship mentioned for the band at 3350 cm ⁻¹ .
3438	Strong	
3475	Weak	
3500	Weak	These bands have been attributed to the presence of various alkali ion impurities [2, 3]. However, we have been unable to find any direct correlation between these bands and the alkali used in the solvent.
3515	Weak	
3555	Weak	
3580	Strong	See note for 3396 above.

differences do exist in the region from 3200 to 3600 cm^{-1} . A summary of frequencies observed in this region is presented in Table 3, and an attempt is made to correlate these bands with those observed in the spectra of natural and other synthetic quartz specimens [2, 3]. Some of these bands have been attributed to overtone or combination bands of Si-O vibrations, while others have been attributed to the presence of various alkali impurities [2, 3]. However, we have not been able to assign any definite band with a specific alkali used as a solvent although this was one of the objectives of this study (see Table 3).

During the course of examining the infrared spectra of a large number of crystals it was observed that an unexpected time- or perhaps temperature-related phenomenon was causing an increase in absorbance in the region 3550–2900 cm^{-1} . The maximum change

occurs at about 3250 cm^{-1} . See Fig. 1. This increase in absorbance was not anticipated and made early attempts to relate extinction coefficients to the various growth parameters difficult. The causal relationship between time (or temperature) and variation in absorbance is being further investigated. We believe that the observed variation in absorbance is due to a change taking place within the crystal and is not the result of condensed water vapor or any other gases. When warmed to room temperature, the crystals return to their original state. Fortunately, the first significant band at 3580 cm^{-1} appears to be largely unaffected by this phenomenon and it was used in the comparisons to be made later. Dodd and Fraser [2] related the extinction coefficient at 3500 cm^{-1} to the anelastic loss for a number of resonator plates and observed a direct relationship between these parameters.

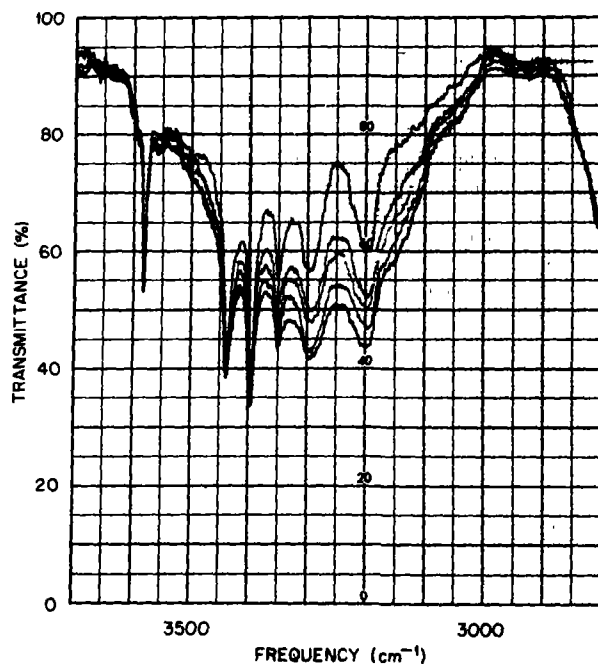


Fig. 1. Effect of time (or temperature) on spectrum of RbOH-grown quartz in region 2900–3550 cm^{-1} . Uppermost curve run one half hour after crystal was placed in holder and liquid nitrogen ($\sim 77^\circ\text{K}$) added. Lowermost curve was run 5 hr afterward. Intermediate curves were run at intermediate times.

(Although the absorbance at 3500 cm^{-1} is affected by time or temperature (Fig. 1), the effect is still relatively small.) The lower the extinction coefficient the lower the anelastic loss. For purposes of comparison with the data of Dodd and Fraser[2], we also determined the extinction coefficient for the background at 3500 cm^{-1} . These values were generally lower than those determined at 3580 cm^{-1} by factors ranging up to five (see Table 1); many of the values are comparable to the best crystals reported by Dodd and Fraser [2]. We prefer the values at 3580 cm^{-1} which are not affected by time (or temperature) as discussed earlier. Plots of extinction coefficient against average growth rate seem to be more clearly related for absorbances determined at 3580 cm^{-1} than for those determined at 3500 cm^{-1} .

4. RELATIONSHIP BETWEEN EXTINCTION COEFFICIENT AND GROWTH CONDITIONS FOR RbOH-GROWN QUARTZ

When the extinction coefficient at 3580 cm^{-1} is plotted against average growth rate a direct relationship can be observed. In determining absorbances the base line was taken tangent to the spectrum at approximately 3650 and 2900 cm^{-1} . The crystals from which the infrared spectra were obtained were grown under a wide variety of experimental conditions of temperature, gradient, pressure, duration, etc. However, among these, nine crystals had duration as the only significant variable. The results are plotted in Fig. 2. A linear relationship between extinction coefficient at 3580 cm^{-1} and average growth is observed if the growth rate is determined for the direction along which the infrared beam was transmitted.

The following explanation is offered to account for the relationship observed between the extinction coefficient at 3580 cm^{-1} and the growth rate expressed in the direction of transmission of the infrared beam. For smaller crystals the beam is passed nearly normal to the AT -cut seed through the entire thickness of grown material. For the larger crystals, the beam is passed at an angle of approximately 35° to the original seed surfaces.

The growth rate of quartz varies with crystallographic direction and is slowest (among the common faces)

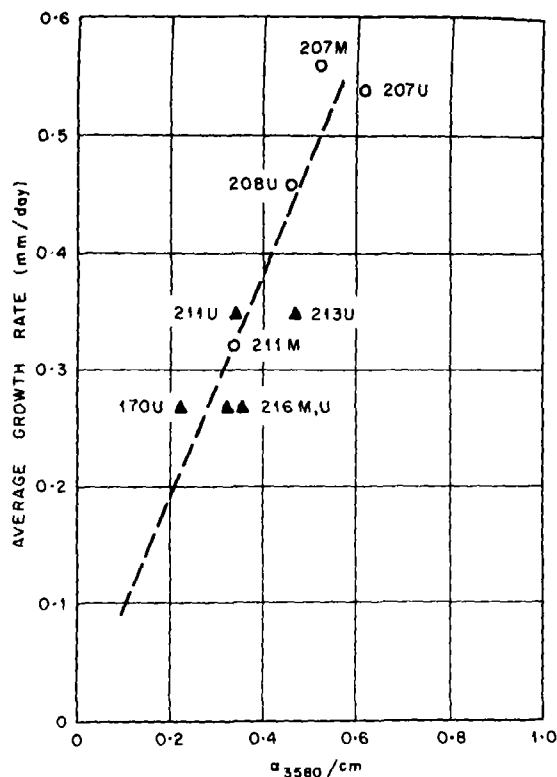


Fig. 2. Linear relationship between growth rate (measured in the direction of transmission of the infrared beam) and α_{3580}/cm for nine crystals grown under nearly identical conditions of temperature and pressure. Slope of line not calculated. It does not necessarily pass through the origin. Symbols used: ○—infrared beam normal to minor rhombohedron; growth rate normal to minor rhombohedron. ▲—infrared beam normal to prism; growth rate normal to prism.

in the direction normal to the prism faces. Hence, when a crystal reaches a thickness normal to the prism determined by the size and orientation of the seed, its apparent growth rate normal to the prism decreases markedly. Note that crystals 170U, 197U, 211U, 213U, 216M, and 216U all have thicknesses normal to the prism of $0.74 \pm 0.03\text{ cm}$ regardless of how much additional material was added normal to the seed. (Crystals 163U and 165U were grown using smaller seeds, but the same argument would apply).

In obtaining the infrared spectra the area through which the beam passes includes the seed, but only a portion of the grown material added on either side of the seed for the larger crystals. Since material added to the rhombohedral ends of such large crystals is not irradiated by the beam and cannot influence the values determined for extinction coefficients, it seems reasonable to exclude

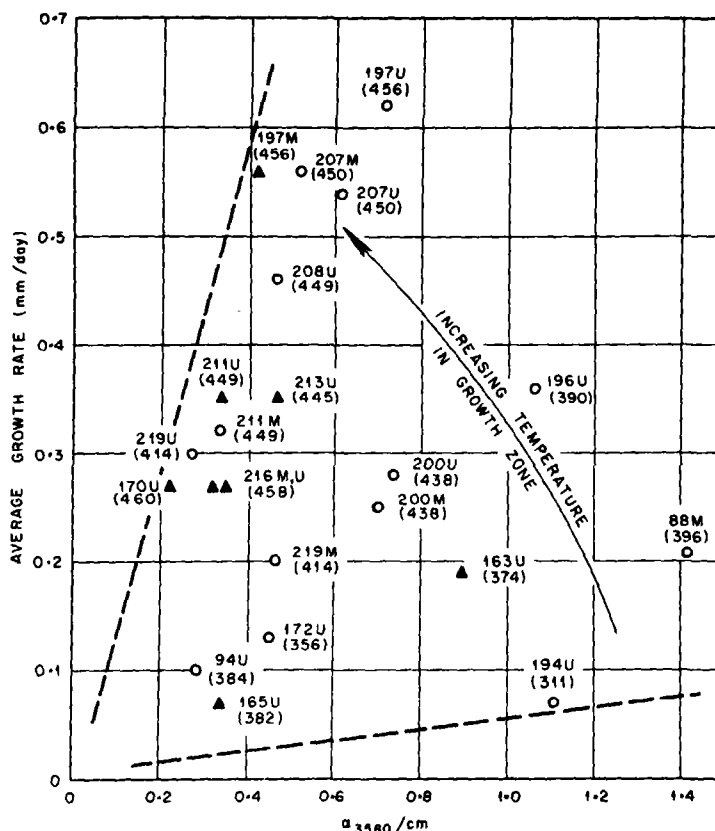


Fig. 3. Plot of relationship between growth rate (measured in the direction of transmission of the infrared beam) and α_{3560}/cm for all the crystals examined in this study. Note the effect of increasing temperature in the growth zone. Boundary lines represent approximate limits of extinction coefficients vs. average growth rates observed in this study. Same symbols as in Fig. 2. Temperature of growth zone in parenthesis.

this material when computing the average growth rate. If average growth rates normal to the minor rhombohedron are used, the values all fall above and to the left of the line shown on Fig. 2.

In addition to excluding the material grown late in the run, using the growth rates normal to the prism serves a second purpose. The beam must pass through layers of added material at an angle of approximately 35° . In determining the growth rate normal to the prism, the growth rate normal to the minor rhombohedron is 'corrected' by the same angular factor. That the effect of determining the extinction coefficient normal to the prism seems to be offset by concomitantly determining the growth rate at that same angle to the minor rhombohedron appears to be borne out by the plot of values shown in Fig. 3.

Obviously, growth rate data for such larger crystals are less accurate because of the change in growth rate

that occurs when the prism faces are developed. However, since an essentially linear fit was observed in Fig. 2, data for these and other large crystals were plotted in Fig. 3. Omission of these data points would not influence the conclusions reached concerning the relationship between extinction coefficient and average growth rate. They are included to demonstrate that extinction coefficients may be determined by passing the beam either normal to the seed or the prism, provided the average growth rate is measured along the same direction.

It was anticipated that crystals grown more rapidly would have higher extinction coefficients; however, an essentially linear relationship was not anticipated since growth rates diminish with time [7, 8].

Two factors seem primarily responsible for the decreasing growth rates during the course of a run. First, the effective ratio of the surface area of the nutrient to the surface area of the growing crystals decreases with time, and second, the solvent normality decreases slightly with time as it becomes incorporated into other phases in the system[7]. It might be added that growth rates are measured linearly, while the addition of material to the growing crystal takes place on a volumetric basis.

When data for all the crystals prepared are plotted (Fig. 3) in a similar manner to Fig. 2, the values at first appear to be scattered. However, when the growth temperatures of the individual crystals are considered, the results fit a reasonable pattern. Crystals grown at higher temperatures have lower extinction coefficients at 3580 cm^{-1} than those grown at the same rate at lower temperatures.

5. CONCLUSIONS

Several conclusions can be drawn from this study. First, and possibly most important (assuming that infrared absorbance measurements are a good indicator of crystalline perfection), RbOH-grown quartz crystals appear to be of high quality. Crystals grown at about 450°C , at rates up to 0.6 mm per day normal to the seed, have α_{3500}/cm less than 0.3, comparable to some of the best crystals reported by Dodd and Fraser[2]. Actual measurement of anelastic losses for RbOH-grown crystals will be necessary to confirm this view.

Second, study of the plot of the extinction coefficients for all RbOH-grown crystals versus their growth rates (Fig. 3) reveals that crystals grown at higher temperatures are significantly better than those grown at lower temperatures for the same growth rate. If this is also true for crystals grown with the typical sodium-based solvents, crystals of comparable perfection could be grown in much less time if higher growth temperatures were used.

Third, the infrared spectrum of quartz in the region 2900 to 3500 cm^{-1} is affected by the length of time that the crystal is held at liquid nitrogen temperature. A study is underway to try to determine the cause of this phenomenon.

Fourth, evaluation of the chemical analyses (Table 2) strongly suggests that the growing crystal preferentially incorporates smaller ions such as Li^+ , Na^+ , and even the relatively large K^+ ion, although these are present in only minor amounts in the RbOH solvent used. In addition, the total amount of iron (added from the liner) plus aluminum (inherited from the nutrient) is approximately equal to the sum of the plus one impurity ions. We are now attempting to grow ultra-high purity quartz, using high purity RbOH solvent and SiO_2 (which contains less than 1 ppm total Fe plus Al) in an inert liner to be used in further studies relating chemical composition with the infrared spectrum and to determine the effects of impurities on physical properties.

REFERENCES

1. BROWN C. S., *Proc. phys. Soc. Lond.* **75**, 459 (1960).
2. DODD D. M. and FRASER D. B., *J. Phys. Chem. Solids* **26**, 673 (1965).
3. KATS A., *Philips Res. Rep.* **17**, 133 (1962).
4. KING J. C., WOOD D. L. and DODD D. M., *Phys. Rev. Lett.* **4**, 500 (1960).
5. KING J. C., BALLMAN A. A. and LAUDISE R. A., *J. Phys. Chem. Solids* **23**, 1019 (1962).
6. BALLMAN A. A., LAUDISE R. A. and RUDD D. W., *Appl. Phys. Lett.* **8**, 53 (1966).
7. KOPP O. C. and CLARK G. W., *J. Crystal Growth* **2**, 308 (1968).
8. LAUDISE R. A., In *Growth and Perfection of Crystals* (Edited by R. H. Doremus, B. W. Roberts and D. Turnbull), p. 458. Wiley, New York (1958).
9. DODD D. M. and FRASER D. B., *Am. Miner.* **52**, 149 (1967).
10. COHEN A. J. and HODGE E. S., *J. Phys. Chem. Solids* **7**, 361 (1958).
11. LAUDISE R. A., BALLMAN A. A. and KING J. C., *J. Phys. Chem. Solids* **26**, 1305 (1965).

ELECTRONIC STATES OF INTERSTITIAL IONS IN ALKALI HALIDE CRYSTALS*

W. BEALL FOWLER and DIANE N. COPE

Department of Physics, Lehigh University, Bethlehem, Penna. 18015, U.S.A.

(Received 15 December 1969)

Abstract—Semicontinuum and continuum models are used to treat the electronic states of interstitial ions and atoms in insulating crystals. The Hartree-Fock-Slater approximation is used to treat the internal structure of the ions, in cases where such structure exists. Three systems are considered, namely, Na^0 in NaI, the U_2 center in KCl, and Ca^+ in KCl. In the second case, our results are somewhat at variance with those of Schechter, and cast some doubt on the vacancy-centered model of the lowest excited state.

1. INTRODUCTION

IN CONTRAST to the large amount of literature extant on substitutional impurity calculations in alkali halide crystals[1], comparatively little theoretical work has been performed on interstitial centers. In fact, most of the experimental work has focused on interstitial hydrogen (the U_2 center)[2], although a fair amount of work has been performed on Z centers[3], thought by some to be interstitial alkaline-earth ions, and recent interest has developed in interstitial Na^0 in NaI[4].

Wang[5] has performed calculations on interstitial Ca^+ in KCl, proposed as a model for the Z_3 center, while more recently Schechter[6] has presented calculations on the U_2 center, using various model potentials. From his work, Schechter has concluded that a vacancy-centered model of the lowest excited state of the U_2 center is tenable.

In this paper, we use both semicontinuum and continuum models to treat three cases: interstitial Na^0 in NaI, Ca^+ in KCl, and H^0 in KCl. In the first two cases, the internal structure of the ions is treated in the Hartree-Fock-Slater approximation, using the computer routine of Herman and Skillman[7].

We find that semicontinuum and continuum

models yield quite different results. We argue that the semicontinuum model is an acceptable theoretical alternative to the continuum model, and conclude that our results on the U_2 center cast doubt on the vacancy-centered model for the lowest excited state. Our results on Ca^+ are in poor agreement with those of Wang, who used a quite different model, and are far from the experimental results for the Z_3 center. We conclude that interstitial Na^0 should have a strong absorption in the near infrared; this result is discussed in connection with the work of Van Sciver *et al.* on the Q center[4].

2. THE SEMICONTINUUM MODEL AND CALCULATIONS

We consider a continuum model to be one in which quantities such as dielectric constant and effective mass are continuous functions of r , while in a semicontinuum model there are discontinuities at some value of r .

While a semicontinuum model was used in a calculation on interstitial Ca^+ by Wang[5], no discussions of its relative merits as compared with continuum models for interstitial systems have appeared.

This has not been the case for substitutional imperfections. Here, although some work has been based on continuum models,

*Research supported in part by a grant from the Office of Naval Research.

it has generally been conceded that the region of space comprising the impurity atom needs special consideration[1]. While the semi-continuum model has been successful in some ways in describing such systems, it is not our intent to defend this model on an absolute basis; clearly, more sophisticated models, such as developed by Wood and Öpik[8], are preferable. Rather, we wish to present it as a reasonable alternative to various continuum models.

It has long been recognized[9] that in impurity calculations special attention must be paid the central-cell region. This fact is indeed the basis of the Hermanson[10] and other dielectric functions used by Schechter. However, it is not clear that this treatment of the central-cell region is complete, or in all cases, correct. For example, in the Hermanson approach, little attention is paid to the electronic polarization energy about the positive charge, an important quantity which can be computed classically[9, 11]. In the semi-continuum approach, on the other hand, this quantity is explicitly included, as is the electron self-energy through the electron affinity.

If one reviews the arguments made in the derivation of the semicontinuum approximation[9, 11, 12], there seems to be no point at which a substitutional impurity is demanded. In fact, using Mott and Gurney's procedure, one can in the interstitial case define an effective cavity radius in terms of the electronic polarization energy. With these remarks in mind, we write down a simple external semi-continuum potential for an electron on an interstitial atom:

$$V(r) = W - \chi \quad r < R_0$$

$$= \frac{e^2}{r} \left(1 - \frac{1}{\epsilon_\infty} \right) \quad r > R_0 \quad (1)$$

where W is the electronic polarization self-energy[9, 11]

$$W = \frac{e^2}{2R_0} \left(1 - \frac{1}{\epsilon_\infty} \right), \quad (2)$$

χ is the electron affinity and ϵ_∞ is the high-frequency dielectric constant.

χ and ϵ_∞ may, in principle, be determined from experiment; the other terms depend on R_0 . R_0 , however, may be obtained from a result of Mott and Gurney[9]; they calculate W for interstitial positions in several crystals, and from their calculated value, R_0 may be obtained.

Their results for W are about the same for NaCl and KCl, and since for the substitutional case the results for NaI are close to those for NaCl and KCl, we take for NaI the same result as for NaCl and KCl, namely, $W = 3.08$ eV. Even with these approximations, the uncertainty in W is less than that in χ ; we took $\chi = -0.04$ a.u. for all cases considered[9].

For NaI, then, where $\epsilon_\infty = 2.93$, R_0 is $2.91 a_0$, smaller than the corresponding number for substitutional impurities.

The potential of equation (1) is shown in Fig. 1. The dashed line represents the potential that one would use in a similar continuum calculation (i.e. $R_0 = 0$). One can note, then, that the semicontinuum external potential is less repulsive than a continuum external potential.

We have also made calculations using other assumptions: (a) equation (1) but with a static dielectric constant; (2) a potential for $r > R_0$ used by Schechter and due to Hermanson[10]; (c) same as (b) but with $R_0 = 0$.

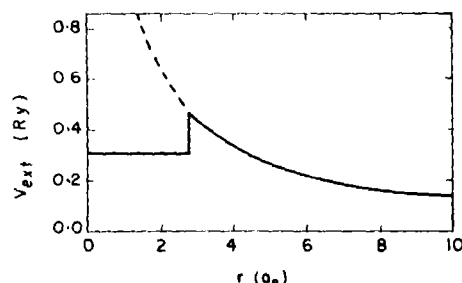


Fig. 1. The potential of equation (1) for an interstitial in NaI (solid line). The dashed line from $r = 0$ to $r = 2.91 a_0$ plus the solid line from $r = 2.91 a_0$ to infinity represents a corresponding simple continuum potential.

We also computed oscillator strengths for the lowest $s \rightarrow p$ transition in several cases.

In the case of Na^0 and Ca^+ , the internal structure of the ions was treated using the Hartree-Fock-Slater approximation with the computer program of Herman and Skillman[7], suitably modified for our problem. This approach has been extensively used in energy band calculations. For these cases of one electron outside a closed shell, we felt it justified to make an invariant core approximation for the lowest excited p state.

3. DISCUSSION

The several external potentials produced rather different results for the cases considered. For NaI, for example, predicted $3s-3p$ transition energies range from 0.4711 to 0.9403 eV, and oscillator strengths from 0.1167 to 0.5908. From an experimental point of view, however, this range is small enough that Na^0 absorption in NaI should be detectable, and the absence[4, 13] of such absorption indicates either that interstitial sodium is not present in particular cases

Table 1. Optical absorption of Na^0 in NaI. Column I contains results obtained with the external potential of equation (1) with a high-frequency dielectric constant; Column II is the same with a static dielectric constant. Column III contains results obtained from Schechter's continuum potential a la Hermanson; Column IV is the same, except for $r < 2.91 a_0$ a constant potential of 0.15 a.u. is used

	I	II	III	IV
Energy { $3s$	-0.09888	-0.03939	-0.04592	-0.07168
(Ryd) { $3p$	-0.02974	-0.00479	-0.01026	-0.01054
$\Delta E(3s-3p)$ eV	0.9403	0.4711	0.4714	0.8315
Oscillator strength	0.5908	0.1167	0.5312	0.3241

Table 2. Optical absorption of H in KCl. Columns I, II, III, IV are labeled as in Table 1. Here $R_0 = 2.34 a_0$

	I	II	III	IV
Energy { $1s$	-0.69983	-0.69039	-0.51731	-0.69295
(Ryd) { $2p$	-0.05899	-0.01187	-0.02716	-0.01147
$\Delta E(1s-2p)$ eV	8.715	9.228	6.666	9.268

We tested these approximations by computing the transition energy and oscillator strength for atomic Na. The results were within 1 per cent of experiment, suggesting that our procedure was acceptable. Results for Na^0 in NaI are shown in Table 1, those for H in KCl in Table 2, and those for Ca^+ in KCl in Table 3.

Table 3. Optical absorption of Ca^+ in KCl. The potential used was of the form of equation (1) with a high-frequency dielectric constant

Energy { $4s$	-0.3372
(Ryd) { $4p$	-0.1921
$\Delta E(4s-4p)$ eV	1.97

where it is expected to be, or the sodium is ionized (Na^+).

For H° , we found transition energies generally higher than those predicted by Schechter [6], and higher than experimentally observed. It might be argued that this invalidates our semicontinuum model, although we feel that this model is tenable. It is interesting to note, from the last column of Table 2, that even when we use the Hermanson potential used by Schechter, we obtain a transition energy higher than Schechter's (and experiment) by about 1.5 eV. We feel that this difference arises because we solved the Schrödinger equation numerically, with rather high accuracy, while Schechter used a variational approach. If the variational approach introduced similar errors in all of his calculations, then all of Schechter's models would when solved more exactly predict a transition energy too large. Thus we feel that, irrespective of the merits of semicontinuum vs. continuum theory, the vacancy-centered model of the U_2 excited state is open to doubt.

For interstitial Ca^+ in KCl, we obtained a transition energy of 1.97 eV, and an oscillator strength very nearly unity, using our semicontinuum model. This result is not very close to that of Wang [5], nor to the experimental absorption energy of the Z_3 center (2.53) [3].

Acknowledgements—We thank Drs. A. Barry Kunz and Wesley J. Van Sciver for helpful discussions.

REFERENCES

1. See, e.g. FOWLER W. B., *Physics of Color Centers* (Edited by W. Beall Fowler), p. 54. Academic Press, New York (1968).
2. DELBECQ C. J., SMALLER B. and YUSTER P. H., *Phys. Rev.* **104**, 599 (1956); KERKHOFF F., MARTIENSSEN W. and SANDER W., *Z. Phys.* **173**, 184 (1963); SPAETH J. M., *Z. Phys.* **192**, 107 (1966); FISCHER F., *Z. Phys.* **204**, 351 (1967).
3. See, e.g. KOJIMA K., *J. phys. Soc. Japan* **19**, 868 (1964).
4. VAN SCIVER W. J., MACK S. A. and FONTANA M. P., *Int. Symp. on Color Centers in Alkali Halides, Rome, Italy* (1968), Unpublished; FONTANA, M. P. and VAN SCIVER, W. J., *Phys. Status Solidi*, To be published.
5. WANG S., *Phys. Status Solidi* **23**, 387 (1967).
6. SCHECHTER D., *Phys. Rev.* **180**, 896 (1969).
7. HERMAN F. and SKILLMAN S., *Atomic Structure Calculations*. Prentice-Hall, Englewood Cliffs, N.J. (1963).
8. ÖPIK U. and WOOD R. F., *Phys. Rev.* **179**, 772 (1969).
9. MOTT N. F. and GURNEY R. W., *Electronic Processes in Ionic Crystals*, 2nd Edn. The Clarendon Press, Oxford, England (1948). Reprinted by Dover, New York (1964).
10. HERMANSON J., *Phys. Rev.* **150**, 660 (1966).
11. FOWLER W. BEALL, *Phys. Rev.* **151**, 657 (1966).
12. SIMPSON J. H., *Proc. R. Soc. Lond.* **A197**, 269 (1949).
13. MACK S. and BATEMAN R., Private communication.

ON THE DICHROISM OF TOURMALINE

M. G. TOWNSEND

Department of Energy, Mines and Resources, Mines Branch, Ottawa, Canada

(Received 17 October 1969; in revised form 5 December 1969)

Abstract—The dichroism of tourmaline arises partially from charge-transfer transitions within next-nearest neighbour cations through shared octahedral edges in the 001 layer. Similar structural features occur in the sheet silicates, and charge-transfer spectra in these structures are discussed.

1. INTRODUCTION

TOURMALINE $\text{Na}(\text{Mg, Fe, Mn})_3\text{Al}_6\text{B}_3\text{Si}_6\text{O}_{27}(\text{OH, F})_4$ has a complex structure[1], but for the purpose of discussing its optical absorption spectrum it is necessary to consider primarily only two octahedral sites, i.e. the *b* site, which can contain Mg, Fe and Mn, and the *c* site, which contains Al[2,3,4].

As shown in Fig. 1 the *b*-site ions lie in trigonal planes perpendicular to the *c* axis,

and the *c*-site ions are displaced by 1-2 per cent of the *c* parameter above these planes. The *b*-site ions are octahedrally coordinated to four oxygen ions, and two hydroxyl groups. These octahedra each share two edges with the adjoining octahedra in the trigonal plane and two edges with *c*-site octahedra. Each *c*-site octahedron also shares two edges with adjoining *c*-site octahedra forming, in effect, spiral chains in the *c*-direction.

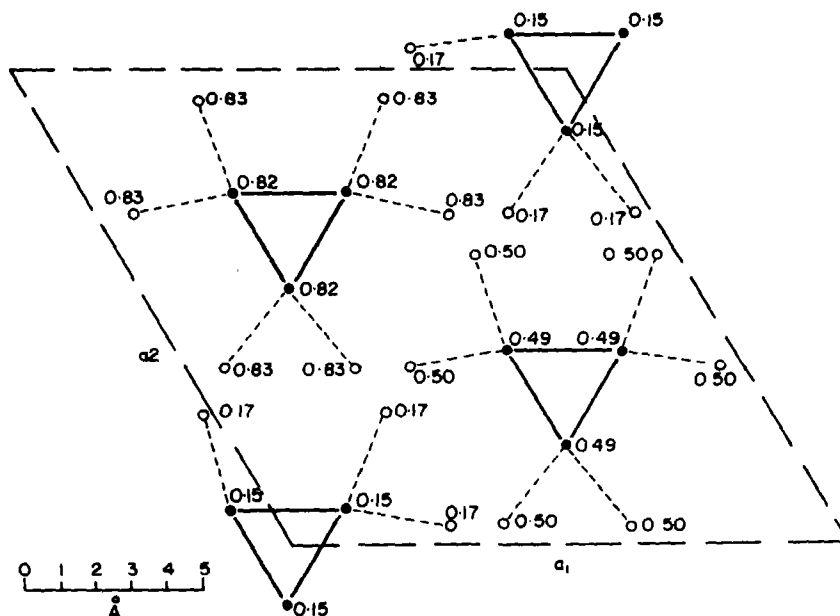


Fig. 1. A (001) projection of (Mg,Fe,Mn) ions (black circles) in *b* sites, and Al ions (open circles) in *c* sites, in tourmaline. Figures indicate fractional distances above the zero plane. Short metal-metal distances, representing directions across shared octahedral edges shown as solid lines between (Mg,Fe)-(Mg,Fe) and as dashed lines between (Mg,Fe-Al) (from Faye[8]).

The structure of dravite $\text{NaMg}_3\text{Al}_6\text{B}_3\text{Si}_6\text{O}_{27}(\text{OH},\text{F})_4$ has been determined accurately [1]. The *b*-site symmetry is C_1 with bond distances $\text{Mg}-(\text{OH}_1)$, 2.063 Å, $\text{Mg}-(\text{OH}_2)$, 2.116 Å, $\text{Mg}-\text{O}$, 2.032 Å [2] and 2.023 Å [2], and bond angles varying from 81–97°. The major distortion is tetragonal along the OH_1-OH_2 axis at an angle of about 63° to the *c* axis. The *c*-site symmetry is also C_1 .

The absorption spectra of pink [3,4], blue [2,3], green [2,3], brown [3,4], Fig. 2, and black tourmaline have been recorded. The brown and black tourmalines fall on the dravite schorl ($\text{Na}(\text{Fe}, \text{Mn})_3\text{Al}_6\text{B}_3\text{Si}_6\text{O}_{27}(\text{OH},\text{F})_4$) join. Wilkins *et al.* [3] assigned two prominent absorption bands in the 9000–14,000 cm^{-1} region to the ${}^5\text{T}_2 \rightarrow {}^5\text{E}$ transition of Fe^{2+} in the *b* site with a tetragonal splitting of ${}^5\text{E}$ of approximately 5000 cm^{-1} . An alternative assignment of the 14,000 cm^{-1} band to an $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ charge-transfer transition was proposed by Faye *et al.* [2]. All u.v., visible and near i.r. bands (apart from

OH vibrational structure) in the tourmaline spectra are markedly dichroic with maximum absorption occurring for $E \perp c$.

The colour and pleochroism of many silicates in which there are layers or groups of edge-sharing octahedra has been attributed in part to $\text{Fe}^{2+}t^4e^2 \rightarrow \text{Fe}^{3+}t^3e^2$ charge-transfer. Such transitions are allowed when *E* is in the plane of the octahedral layers containing the Fe inter-nuclear vector [2,5–7].

In the present work the origin of the dichroism of the tourmaline u.v. bands is considered using a qualitative one electron molecular-orbital energy level scheme. The nature of the visible dichroism and band splitting is shown to be consistent with the C_1 point group of the *b* and *c* sites

2. DISCUSSION

It seems likely that the visible absorption band in the 14,000 cm^{-1} region in tourmaline arises from the *d-d* $\text{Fe}^{2+} {}^5\text{T}_2(t^4e^2) \rightarrow {}^5\text{E}(t^3e^3)$ transition, rather than from an $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$

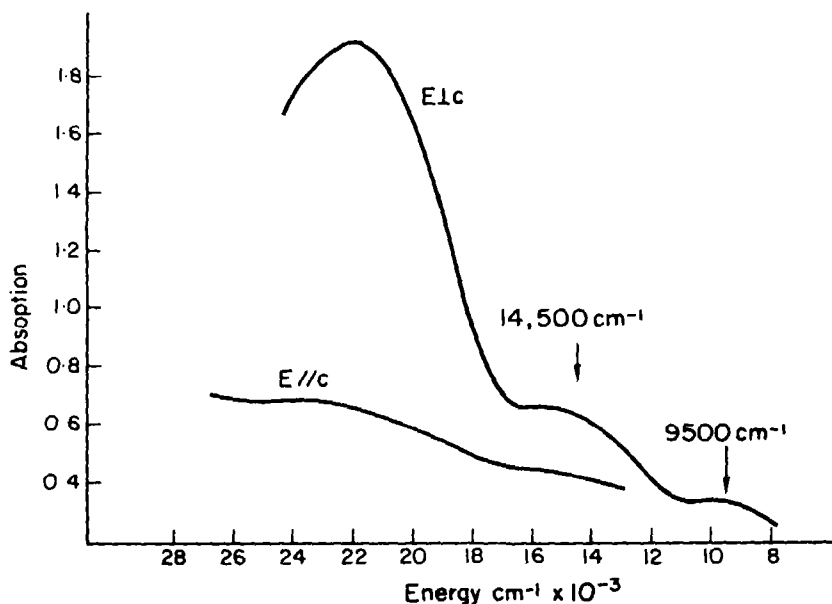


Fig. 2. Polarised absorption spectrum of dravite recorded at room temperature (from Manning, 1969).

charge transfer transition since the ratio of intensity of this band and the 9000 cm^{-1} band remains approximately constant in a range of tourmalines of varying $\text{Fe}^{2+}/\text{Fe}^{3+}$ concentration [3, 8]. An alternative suggestion [3] for the origin of this splitting, as the dynamical Jahn-Teller effect, may readily be discounted. This interaction raises the degeneracy of the ${}^5\text{E}$ term in octahedral symmetry; a splitting of 5000 cm^{-1} would be equivalent to a Jahn-Teller energy of $\sim 4\text{ eV}$ whereas a typical Jahn-Teller energy of an 'e' hole is 0.5 eV [9].

Since a strong $\text{Fe}^{2+}(t^4e^2) \rightarrow \text{Fe}^{3+}(t^3e^2)$ charge-transfer absorption ($f \sim 10^{-3}$) occurs at $\sim 14\text{--}18,000\text{ cm}^{-1}$ in other ferromagnesian silicates with intercationic distances of similar magnitude, the absence or low intensity of this band in tourmaline points to a low concentration of adjacent $\text{Fe}^{2+}\text{--}\text{Fe}^{3+}$ ion pairs. There is a strongly dichroic absorption shoulder at $17,500\text{ cm}^{-1}$ in the spectra of certain blue-green tourmalines, and this may well represent $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ interaction [8].

Wilkins *et al.* [3] did not discuss the dichroism of the tourmaline u.v. bands, but suggested that the $\text{Fe}^{2+} {}^5\text{T}_2 \rightarrow {}^5\text{E}$ transition borrowed intensity from these bands through the odd terms in a series expansion of the crystalline field. They noted that crystalline field splittings are due to even and odd terms, whilst intensities are due only to odd terms, with the major portion due to the largest odd terms. Analysing the coordination of the metal ions they considered that the largest odd field term was a trigonal field in the (111) direction of the b octahedron, almost coinciding in direction with the c -axis of the lattice. From this, in spite of the large tetragonal splitting of the ${}^5\text{E}$ term, they attempted to describe the intensity borrowing by using C_3 symmetry for the b octahedron.

In discussing this model it firstly should be made clear that whilst the (111) axis of the b or c octahedron is almost parallel to the c -axis direction, it is not coincident with the 3 fold symmetry c -axis. The latter is situated at the centre of the brucite triangle not on one of the

b or c site cations, Fig. 1. If a Hamiltonian is constructed from Wilkins model we obtain, $\mathcal{H} = \mathcal{H}_{\text{cubic}} + \mathcal{H}_{\text{odd-trigonal}} + \mathcal{H}_{\text{even-tetragonal}}$ and evidently neither this Hamiltonian nor its eigen vectors transform according to the operations of the C_3 group. Because of the high distortion of the b or c octahedron, termination of the series expansion of the crystalline field at terms linear in the distortion parameter, ignoring even and higher order odd terms, which in effect is equivalent to Wilkins concept of a pseudo-trigonal field, would appear to be a poor approximation.

Since there is no unique axial distortion of the b or c octahedron along the c -axis direction, the observed dependence of the absorption intensity on the relative orientation of the electric vector with respect to the c axis must arise either from next-nearest neighbour interaction or from the symmetry in the composite absorption of the $3b$ and $6c$ sites about the 3 fold axis at the centre of the brucite triangle, Fig. 1. The latter contributes to the dichroism if transitions within individual b -site octahedra are polarised, e.g. along the $\text{OH}_1\text{--}\text{OH}_2$ tetragonal axis at 63° to the c -axis. The resultant absorption from 3 different b sites is then polarised with respect to the c -axis, and the ratio of absorption intensity (α) for $E \parallel$ or $\perp c$ is $1 \leq \alpha \leq 1.73$. Similarly the composite absorption from the 6 c -sites and the 6 silica tetrahedra in the hexagonal ring centred on the c -axis in the 001 plane below the brucite triangle, may also contribute to the dichroism; the latter through polarisation of $\text{O}^{2-} \rightarrow \text{Si}$, $3s$, $3p$, u.v. transitions within the silica tetrahedra. These contributions give most intense absorption, for a particular transition, for $E \parallel$ or $\perp c$ depending on the anisotropy of the lattice phonon interaction and sign of the crystal field splitting.

Next-nearest neighbour interaction on the other hand unambiguously leads to maximum absorption for $E \perp c$. Figure 1 shows that the number of possible pair interactions between next-nearest neighbour ions in b and c sites in the 001 plane outnumbers the interactions

at approximately 60° to the 001 plane in the *c*-site spiral chain by 2 : 1.

Some evidence for next-nearest neighbour interaction in dravite has been noted by Manning[4]. He assigned a prominent markedly dichroic absorption band at $22,000\text{ cm}^{-1}$ in dravite containing 1.15% Ti, Fig. 2, to the charge-transfer transition $\text{Ti}^{3+} \rightarrow \text{Ti}^{4+}$. Many intervalence charge-transfer transitions have been observed in the solid state[5,6,10,11] and this type of transition is now discussed.

Mulliken[12] has derived an approximate expression for the oscillator strength of a charge-transfer transition. The wave functions of the isolated donor and acceptor ions are denoted Ψ_d and Ψ_a respectively. Mixing of these gives the more general wavefunctions.

$$\begin{aligned}\Psi_{d'} &= \Psi_d + \lambda_{ad} \Psi_a \\ \Psi_{a'} &= \Psi_a + \lambda_{da} \Psi_d\end{aligned}$$

$\Psi_{d'}$ and $\Psi_{a'}$ are orthogonal giving $S_{ad} = -(\lambda_{ad} + \lambda_{da})$ where $S_{ad} = \langle \Psi_{d'} | \Psi_{a'} \rangle$. The electric dipole oscillator strength, $f_{d'a'}$, for transitions from $\Psi_{d'} \rightarrow \Psi_{a'}$ is given by:

$$f_{d'a'} = 1.085 \times 10^{-5} \nu (Ed'a')^2 - (i)$$

where $Ed'a' \approx E_{da} + e\lambda_{da}r_{ad}$, e is the electronic charge, r_{ad} the internuclear distance, ν the transition frequency and E_{da} the electric dipole moment, $\langle \Psi_d^* | r | \Psi_a \rangle$.

Robin[11] has calculated the degree of delocalisation between donor $\text{Fe}^{2+}(t^6)^1A_1$ ground state and acceptor $\text{Fe}^{3+}(t^3e^2)^6A_1$, excited state from the observed oscillator strength in cubic Prussian Blue. He assigned the observed strong band at $14,000\text{ cm}^{-1}$ to a $t_{2g} \rightarrow t_{2g}$ transition and the weaker band at $24,000\text{ cm}^{-1}$ to a $t_{2g} \rightarrow e_g$ transition. He pointed out that, because of local orthogonality between the $\text{Fe}^{2+}t_2$ and $\text{Fe}^{3+}e_g$ orbitals, the $t_{2g} \rightarrow e_g$ transition is forbidden to first order.

In tourmaline and many of the sheet silicates, adjacent octahedrally coordinated cations share octahedral edges, resulting in trigonal brucite-like fragments throughout the

structure. Figure 3 shows a portion of the trigonal brucite unit, where M_1 and M_2 are in *b* sites, and may be two similar or different transition metal ions of the same or different valencies, one transition-metal ion and one Al^{3+} or Mg^{2+} ion, or two Al^{3+} or Mg^{2+} ions. Figure 4 shows a qualitative molecular-orbital energy level scheme for the brucite fragment assuming initially an idealised C_{2v} symmetry, where both M_1 and M_2 are transition-metal ions. The depicted relative order of the low-symmetry splittings of the molecular orbital levels is quite arbitrary but does not affect in any way our general conclusions. Energy splittings from metal-metal interaction occur in second order and are negligibly small, whilst orbital admixture is a first-order interaction and contributes to the intensity of intercation charge-transfer transitions.

As an example we consider an M_1 donor ion in a *b* site with ground state predominantly of $3dxy$ symmetry. The discussion applies equally to ions in *c* sites. The $2p$ orbitals of the bridging oxygen ions, Figs. 3,4 form $2A_1$ and $2B_1$ molecular orbitals. $1A_1$ and $1B_1$ π bond with $3dxy$ M_1 and the other orthogonal pair with $3dxy$ M_2 . Consequently, in this case for 90° bonding as approximated by tourmaline and many silicates, metal-ligand-metal overlap is zero.

The σ -bonded $t_{2g}dxy$ orbitals of the M_1 and M_2 ions, Fig. 3, are symmetric with respect to a 2-fold rotation about the M_1 - M_2 internuclear vector. As a result, transition[1] Fig. 4 is allowed, $f \sim 10^{-3}$, for the symmetrical electric-dipole vector component, i.e. for $E||$ the internuclear vector. Similarly for π -bonded antisymmetrical orbitals the moment is non-zero for $E||M_1$ - M_2 . Values of overlap, dipole moment and approximate oscillator strength computed in the tourmaline lattice for $M_1 = \text{Fe}^{2+}$, $M_2 = \text{Fe}^{3+}$ using simple analytical wavefunctions[13] are listed in Table 1.

The $t_2 \rightarrow e$ forbidden transition[2] has not been observed in silicates but recently[6] a weak absorption band in partially oxidized

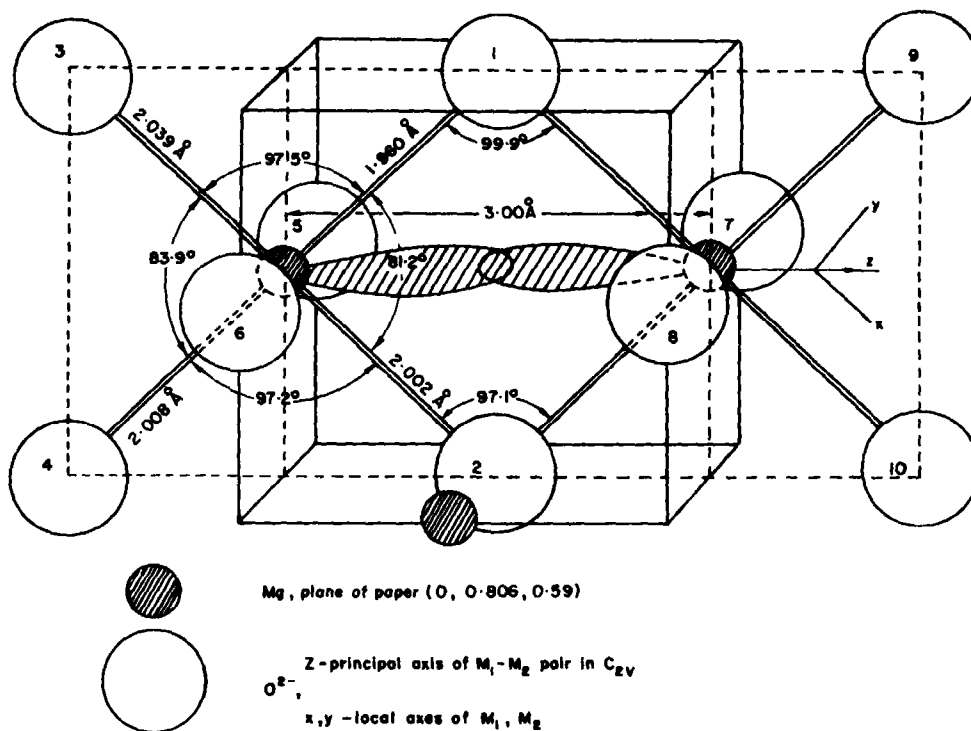


Fig. 3. Fragment of the trigonal brucite unit of tourmaline, showing 3 Mg *b* sites. One *dxy* orbital lobe is shown on each of two of the cations.

vivianite in the $24,000\text{ cm}^{-1}$ energy region, polarised for $E \perp M_1-M_2$, has been assigned to this transition. In vivianite, the symmetry of a pair of Fe^{2+} and Fe^{3+} ions sharing an octahedral edge in site (2) is C_{2v} where the *b* axis is the principal 2-fold symmetry axis. In this point group the $t \rightarrow e$ transition is no longer strictly forbidden and may occur, for $E \parallel$ or $\perp M_1-M_2$ since the $3d_{t_2}$ and $3d_e$ configurations are split into A_1, A_2, B_2 and A_1, B_1 respectively, with the $3d_{t_2}A_1$ and $3d_eA_1$ admixed in the crystal field. The selection rules for $t_2 \rightarrow e$ intercationic transitions are then $A_1 \rightarrow A_1 - E \parallel b$ and $A_1 \rightarrow B_1, B_2 \rightarrow A_1, A_2 \rightarrow B_1 - E \perp b$, and if the assignment is correct the Fe^{2+} donor orbital ground-state must necessarily be of B_2 or A_2 symmetry.

Transition [3] Fig. 4 between σ -bonded $M_1 3dxyA_1^*$ and $M_2 4sA_1^*$ is allowed, $f \sim 10^{-3}$,

for $E \parallel M_1-M_2$ in contrast to transition (6) $M_1 3d \rightarrow M_1 4s$ which is parity forbidden. Transition (4) $3dxy \rightarrow 4px, 4py$, $f \sim 10^{-2}$ is allowed for $E \parallel M_1-M_2$ through metal-ligand-metal π - σ overlap and direct metal-metal σ overlap. The former is less than one half of the latter, 0.125, in tourmaline. Transitions [7], [8] and [9] are strong oxygen $\rightarrow$ metal transitions, $f \sim 10^{-1}$, allowed for both $E \parallel M_1-M_2$ and $E \perp M_1-M_2$. Due to mixing of $M_2 4s$ and $4p$ orbitals in the B_1, A_1 bridging 0.1-2 bonding orbitals, some of the intensity of [7] arises from the integral $\langle M_1^* | E | M_2 \rangle$. Thus transition [7] should be partially polarised with maximum absorption occurring for $E \parallel M_1-M_2$. Similarly, transitions (3) and (10) will be partially polarised due to overlap of $M_1 4p, 4s$ and $M_2 4p, 4s$ orbitals. The energy of $t \rightarrow t$ charge-transfer transitions between

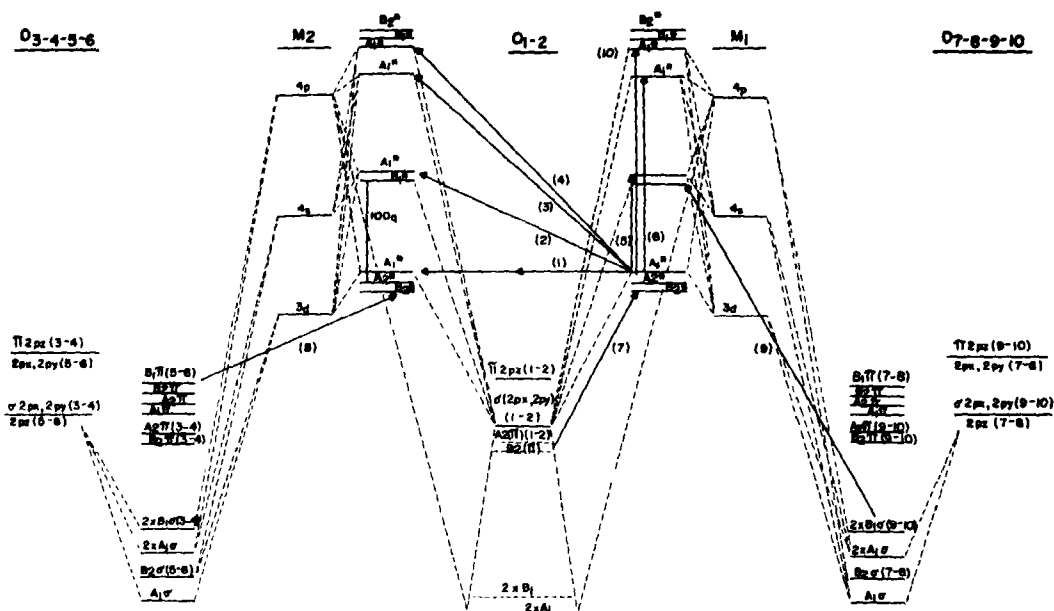


Fig. 4. Molecular-orbital scheme for the brucite unit with M_1 and $M_2 3d$ transitional metal ions in b sites. Molecular orbitals of the bridging O_{1-2} atoms are shown in the centre of the diagram below the atomic orbitals. Some possible transitions [1-10] are indicated.

identical ions i.e. $Fe^{3+} \rightarrow Fe^{3+}$, is absorbed completely by the lattice phonons. Partial absorption of the transition energy by phonon modes results in transitions [2-4] being generally of higher energy than the corresponding intra-cationic transitions [5, 6 and 10].

We make no attempt to relate the calculated higher energy charge-transfer transitions to experiment since detailed experimental data in this energy region are almost non-existent. The results of Table 1 should not differ greatly for any combination of transition-metal ions, and infer generally that the $M_1 \rightarrow M_2$ transitions as discussed here contribute significantly to the observed u.v. dichroism. The point group C_1 of the M_1 site does not contain the inversion operation, and consequently, crystal-field mixing of the $M_1 3de$ states with excited states of transitions [2-4, 7-10] partially polarises the visible $Fe^{2+} 5T_2(t^4e^2) \rightarrow 5E(t^3e^3)$ transition (i.e. when $M_1 = Fe^{2+}$) giving maximum intensity for $E || M_1-M_2$.

The marked dichroism of the u.v. and visible spectrum of colourless tourmaline, Fig. 5, where no more than 0.1 and 0.2 per cent of the total available $b+c$ sites are occupied by Fe and Mn respectively*, may result either from statistical distribution of the Fe and Mn in the $3b$ and $6c$ sites, and subsequent polarisation of the combined absorption about the c -axis as discussed earlier, or alternatively from Mn and Fe transitions terminating on Al^{3+} or $Mg^{2+} 3s, 3p$ excited states.

Contrasting optical properties are shown by the monoclinic amphiboles where there are strips of octahedrally coordinated Fe atoms in the $b.c.$ plane [14]. At right angles in the $a.c.$ plane the visible $Fe^{2+} \rightarrow Fe^{3+}$ and u.v. charge transfer bonds are strongest for E at approximately 10° from the component of the $Fe^{2+} - Fe^{3+}$ internuclear vector $||c$ [14]. This results from the polarisation of the $O_{2-}Fe^{2+}, Fe^{3+}$ u.v. bands about the 2-fold symmetry b axis and an axis in the ac plane 10° from c determined primarily by the distortion of the

Table 1

ψd	ψa	Transition	$\langle \psi d^* \psi a \rangle$	$\langle \psi d^* r \psi a \rangle$	$f/1.085 \times 10^{-3}$	ν	f
$3dxy M_1$	$3dxy M_2$	[1]	0.032	0.097	$(3\lambda_1 + 0.097)^2$	$1.4 \times 10^4 \text{ cm}^{-1}$	$\sim 10^{-3}$
$3dxy M_1$	$4s M_2$	[3]	0.054	0.155	$(3\lambda_2 + 0.155)^2$	$\sim 5 \times 10^4 \text{ cm}^{-1}$	$\sim 10^{-3}$
$3dxy M_1$	$1/\sqrt{2}(4px + 4py) M_2$	[4]	0.125	0.346	$(3\lambda_3 + 0.346)^2$	$\sim 10^5 \text{ cm}^{-1}$	$\sim 10^{-2}$
$1/\sqrt{2}(2px + 2py)$ $(O_{1-2}) A_1$	$3dxy M_1$	[7]	0.346	0.79	$(1.9\lambda_4 + 0.79)^2$	$\sim 3 \times 10^4 \text{ cm}^{-1}$	$\sim 10^{-1}$

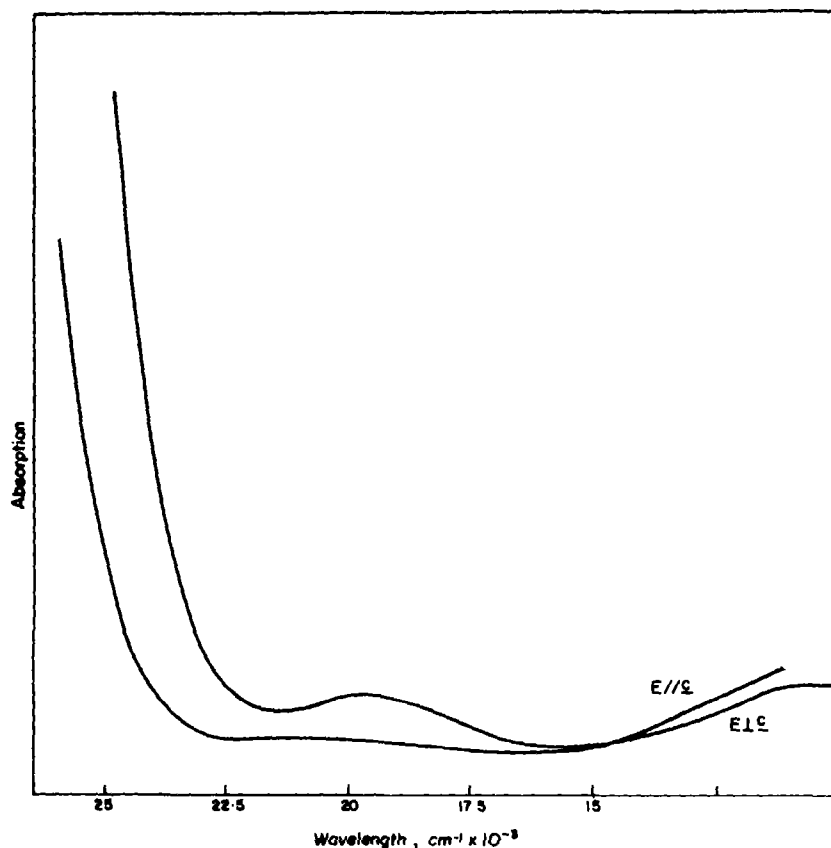


Fig. 5 Polarised absorption spectrum of colourless tourmaline with 0.1 and 0.2 per cent of the available *b* and *c* sites occupied by Fe and Mn respectively, recorded at room temperature, by G. H. Faye.

Fe^{2+} , Fe^{3+} oxygen octahedra. The sense of polarisation of the $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ transition is determined in this case by intensity borrowing of the latter from the u.v. bands.

Acknowledgements—The author thanks G. H. Faye for invaluable discussion, and for recording the spectrum of colourless tourmaline, Fig. 5, and D. C. Harris* for crystal analyses using an electron microprobe.

REFERENCES

1. BUERGER M. J., BURNHAM C. W. and PEACOR D. R., *Acta cryst. all. gr.* **15**, 583 (1962).
2. FAYE G. H., MANNING P. G. and NICKEL E. H., *Am. Miner.* **53**, 1174 (1968).
3. WILKINS R. W. T., FARRELLE E. F. and NAIMAN C. S., *J. Phys. Chem. Solids* **30**, 43 (1969).
4. MANNING P. G., *Can. Mineralogist* **9**, 678 (1969).
5. WEYL W. A., *J. phys. colloid Chem.* **55**, 507 (1951).
6. ALLEN G. C. and HUSH N. S., *Progr. inorg. Chem.*, **8**, 357 (1967).
7. FAYE G., *Can. Mineralogist* **9**, 403 (1968).
8. FAYE G., private communication.
9. STURGE M. D., *Solid St. Phys.* **20**, 91 (1967).
10. TOWNSEND M. G., *Solid-State Commun.* **6**, 81 (1968).
11. ROBIN M. B., *J. inorg. Chem.*, **1**, 337 (1962).
12. MULLIKEN R. S., *J. phys. Chem.* **56**, 801 (1952).
13. RICHARDSON J. W., POWELL R. R. and NIEUWPOORT W. C., *J. chem. Phys.* **38**, 796 (1963).
14. FAYE G. and NICKEL E. H., *Am. Miner.* (In press).

THE EPR SPECTRUM OF TRIVALENT TITANIUM IN ORTHORHOMBIC SYMMETRY IN MgO*

J. J. DAVIES† and J. E. WERTZ

Department of Chemistry, University of Minnesota, Minneapolis, Minn. 55455, U.S.A.

(Received 5 December 1969)

Abstract—An orthorhombic EPR spectrum is observed in titanium-doped MgO at 20°K and lower temperatures. The effective electronic spin $S = \frac{1}{2}$, and the principal g factors are:

$$\begin{aligned}g_A[110] &= 1.8487 \pm 0.0007 \\g_Y[\bar{1}10] &= 1.9464 \pm 0.0007 \\g_Z[001] &= 1.7670 \pm 0.0007.\end{aligned}$$

Hyperfine structure due to $^{47,49}\text{Ti}$ is observed with the magnetic field in the z direction; for this direction the hyperfine coupling constant $A_z = 12.5 \times 10^{-4} \text{ cm}^{-1}$. The titanium ion is ascribed to the trivalent state; the orthorhombic symmetry is ascribed to association with a positive-ion vacancy in the $[110]$ or $[\bar{1}10]$ direction.

1. INTRODUCTION

PARAMAGNETIC centers of tetragonal symmetry have previously been reported in titanium-doped magnesium oxide [1, 2]. Observation of ^{47}Ti and ^{49}Ti hyperfine structure [2] unambiguously identified the element responsible, and the effective spin $S = \frac{1}{2}$ established the trivalent state for the $(3d^1)$ titanium ions. We report here an additional electron paramagnetic resonance (EPR) spectrum, observed at 20°K and lower temperatures in Ti-doped MgO. This spectrum also corresponds to $S = \frac{1}{2}$, but it shows orthorhombic symmetry; it is considerably more intense than the tetragonal spectrum observed at 77°K.

2. EXPERIMENTAL PROCEDURES AND RESULTS

Titanium-doped magnesium oxide crystals grown by the arc-fusion method were obtained from the General Electric Company: the melt contained 2 per cent by weight of TiO_2 . The

specimens used were the same as those in Ref. [2]. An X-band (9.4 GHz) recording of the EPR spectrum taken at 20°K with the external magnetic field along the $\langle 100 \rangle$ crystal axis is shown in Fig. 1. The dominant lines arise from:

- (a) Mn^{2+} and Cr^{3+} impurities.
- (b) A center with orthorhombic symmetry and effective spin $S = \frac{1}{2}$. The lines from this center are denoted by R_1 and R_2 .
- (c) Centers of symmetry lower than orthorhombic, which give sets of lines in the region 3400–3900 G.

Rotation of the magnetic field in the (001) and (011) crystal planes establishes the orthorhombic symmetry of spectrum (b). The line positions at three microwave frequencies (9.4, 17.5 and 35 GHz) can be described by an effective electronic spin $S = \frac{1}{2}$. The spin Hamiltonian may therefore be written:

$$\mathcal{H} = g_Z \beta S_Z H_Z + g_X \beta H_X S_X + g_Y \beta H_Y S_Y.$$

The Z -axis is taken along an $[001]$ crystal direction, X along $[110]$ and Y along $[\bar{1}10]$; the relative choice of X and Y is arbitrary.

*This research was supported in part by the U.S. Air Force Office of Scientific Research under Grant No. AFOSR-69-1692.

†Present address: Department of Physics, University of Hull, England.

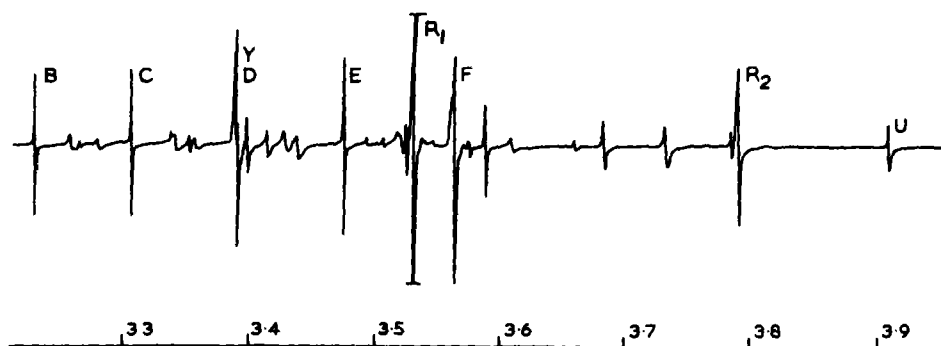


Fig. 1. The X-Band EPR spectrum of a MgO:Ti crystal at 20°K. The magnetic field is along an [001] direction. The lines R_1 and R_2 arise from a Ti^{3+} center with orthorhombic symmetry. Lines B through F denote five of the six octahedral $M = \frac{1}{2} \leftrightarrow -\frac{1}{2}$ hyperfine components of Mn^{2+} . Y denotes a Cr^{3+} line. U denotes a low-symmetry titanium line (see text).

The g factors for the principal crystal directions are given in Table 1. These values are measured relative to the g -value of DPPH , taken as 2.0036 ± 0.0003 ; they are seen to be self consistent to well within the uncertainty of the g factor of the reference. At 20°K we find:

$$\begin{aligned} g_x &= 1.8487 \pm 0.0007 \\ g_y &= 1.9464 \pm 0.0007 \\ g_z &= 1.7670 \pm 0.0007. \end{aligned}$$

The effective spin $S = \frac{1}{2}$ and the known high concentration of titanium suggest that the ion responsible for the spectrum is Ti^{3+} . Attempts were made to observe hyperfine structure due to the magnetic isotopes ^{47}Ti (nuclear spin $\frac{5}{2}$, natural abundance 7.3 per cent) and ^{49}Ti (nuclear spin $\frac{3}{2}$, natural abundance 5.5 per cent). The ratios of nuclear moments to nuclear spin for the two isotopes are almost identical[3]; hence the inner six of the eight ^{49}Ti hyperfine components are expected to coincide with the six components of ^{47}Ti ; the predicted intensities of the hyperfine satellites as percentages of the intensity of the central (even isotopes) line are 0.8, 2.3, 2.3, 2.3, 2.3, 2.3, 0.8. In practice, unfortunately, the large number of intense lines precludes investigation of hyperfine structure unless the magnetic field is

along the Z -axis of the center (corresponding to line R_2 of Fig. 1). The g factor here has its minimum value, and this line is well separated from others. Experiments at each of the three microwave frequencies showed evidence of hyperfine satellites of the correct intensity, with spacing of about 15 G, as shown in Fig. 2.

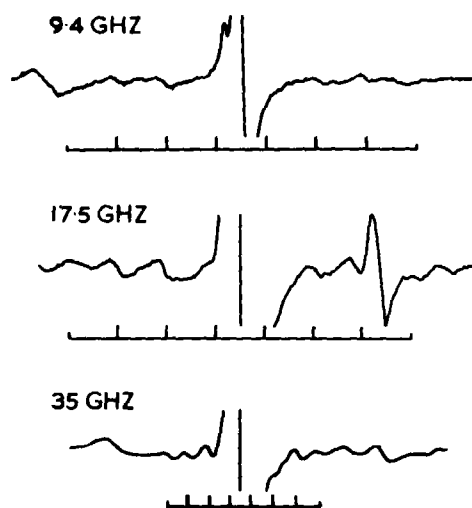


Fig. 2. $^{47,49}\text{Ti}$ hyperfine structure at three microwave frequencies for the g_z line (field along Z -axis of the center). The values of the hyperfine coupling A_z are respectively 15.5 ± 1 , 15.5 ± 1 , 14.5 ± 1.5 G. The 35 GHz sweep is non-linear, owing to magnet saturation. Magnetic fields increase towards the right.

Table 1. Measured and calculated g factors for the orthorhombic center in MgO at X-band and 20°K

Crystal axis	Factor	g-Factors	
		Measured value	Calculated value
$\langle 110 \rangle$	g_x	1.8487	
	g_y	1.9464	
	$\left\{ \frac{g_x^2}{4} + \frac{g_y^2}{4} + \frac{g_z^2}{2} \right\}^{1/2}$	1.8339	1.8338
$\langle 100 \rangle$	g_z	1.7670	
	$\left\{ \frac{g_x^2}{2} + \frac{g_y^2}{2} \right\}^{1/2}$	1.8979	1.8982
$\langle 111 \rangle$	$\left\{ \frac{2g_x^2}{3} + \frac{g_z^2}{3} \right\}^{1/2}$	1.8218	1.8219
	$\left\{ \frac{2g_y^2}{3} + \frac{g_z^2}{3} \right\}^{1/2}$	1.8884	1.8885

The hyperfine coupling constant for the Z-direction of the orthorhombic spectrum is therefore

$$|A_z| \approx 12.5 \times 10^{-4} \text{ cm}^{-1}.$$

The large number of lines of low symmetry have not been analyzed in detail. $^{47,49}\text{Ti}$ hyperfine structure is readily observed on those lines which are sufficiently well separated from other signals (e.g. line *U* of Fig. 1). Experiments at 9.4 GHz and at 35 GHz show, however, that these spectra cannot be described by $S = \frac{1}{2}$; indeed, there is little correspondence between the low-symmetry spectra which are observed at these two frequencies. There appear to be several distinct centers, in some of which the only symmetry property appears to be reflection in an (011) plane.

3. DISCUSSION

The tetragonal spectrum observed at 77°K was identified as originating from the center $\text{Ti}^+ - \text{O} - [=][1, 2]$; in this representation only deviations from the normal site charge are shown; the brackets denote a magnesium vacancy. Centers of this structure have previously been reported for Cr^{3+} [4], Mn^{4+} [5] and Fe^{3+} [6]; the cation vacancies provide compensation for the excess positive charges

on the impurity ions. For $\text{Cr}^{3+}:\text{MgO}$, charge compensation is believed also to occur through formation of the orthorhombic centers indicated in Fig. 3(a)[7]. Since the titanium impurity in the present samples was originally introduced in the tetravalent state (as TiO_2), a large number of positive ion vacancies are expected. Thus a Ti^{3+} center such as that of Fig. 3(b) could be responsible for the spectrum reported in this paper. We discuss this possibility below.

Figure 4 shows the energy levels of a Ti^{3+} ion in an octahedral field. The notation is that of Griffith[8]. A vacancy in the [110] direction (the direction $x = y$ of Fig. 3(b)) would reduce the site symmetry to C_{2v} , removing the degeneracy of the octahedral levels. If the effect of the vacancy is small compared with that of the original octahedral field, the levels will split as shown in Fig. 4(b). The states $|\zeta\rangle$ and $|\theta\rangle$ are mixed by the orthorhombic components of the crystal field; this is represented by writing the eigenfunctions as

$$\begin{aligned} |a\rangle &= |\zeta\rangle \cos \phi + |\theta\rangle \sin \phi \\ |b\rangle &= |\theta\rangle \cos \phi - |\zeta\rangle \sin \phi \end{aligned}$$

where $\cos \phi = 1$ for octahedral symmetry.

For small orthorhombic field components the ground state will be $2^{-1/2}(|\xi\rangle + |\eta\rangle) =$

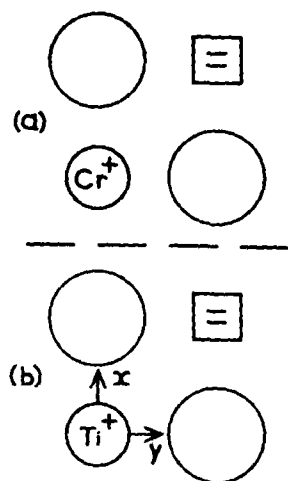


Fig. 3 (a) The orthorhombic Cr^{3+} center reported in Ref. [7]. Only deviations from normal site charge are shown in the diagram. Large circles represent O^{2-} , while the square indicates a magnesium vacancy. (b) Possible model for the Ti^{3+} spectrum reported in this paper. The axes x, y are those used in Ref. [8] to describe the octahedral basis functions. They should not be confused with the experimental axes X, Y , in which X and Y lie along $[110]$ or $[1\bar{1}0]$ crystal directions.

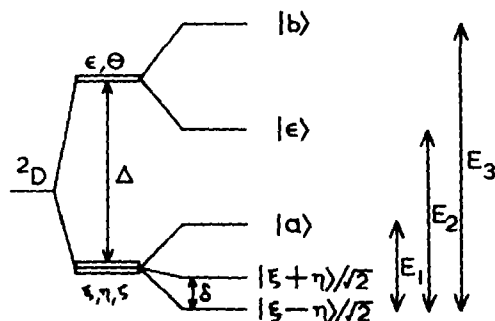


Fig. 4. Energy levels of a $3d$ electron in (a) an octahedral field and (b) an octahedral field with small orthorhombic component produced, for example, by a vacancy on the line $x = y$ of Fig. 3(b). The figure is not drawn to scale. Our experiments cannot distinguish between $2^{-1/2}(|\xi\rangle + |\eta\rangle)$ and $2^{-1/2}(|\xi\rangle - |\eta\rangle)$ as ground states; hence the two lowest levels may be interchanged (see text).

ψ_+ , $2^{-1/2}(|\xi\rangle - |\eta\rangle) \neq \psi_-$, or $|a\rangle$. We may eliminate $|a\rangle$ as a possible ground state by considering the hyperfine interaction. Expressions for A_z may be obtained by using

the methods of Abragam and Pryce [9]. With ψ_+ or ψ_- as the ground state we find

$$A_z = P(-\kappa + \frac{2}{7})$$

while for $|a\rangle$:

$$A_z = P\{-\kappa - \frac{4}{7}(\cos^2 \phi - \sin^2 \phi)\}.$$

Spin-orbit coupling admixtures have not been included (see below). Here $P = 2\gamma_n\beta\beta_n\langle r^{-3} \rangle_{3d}$ and κ represents the core polarization constant (e.g. Ref. [8]); the values found for the tetragonal Ti^{3+} center [2] will be used; thus:

$$\kappa = 0.72 \pm 0.05, |P| = (19.3 \pm 1.0) \times 10^{-4} \text{ cm}^{-1}.$$

For ψ_+ or ψ_- , the predicted value of $|A_z|$ is then $8.3 \times 10^{-4} \text{ cm}^{-1}$. For $|a\rangle$ the value of $|A_z|$ is $(2.9 + 22 \cos^2 \phi) \times 10^{-4} \text{ cm}^{-1}$. Since $\cos^2 \phi$ is expected to approach unity, the experimental value of about $12.5 \times 10^{-4} \text{ cm}^{-1}$ suggests that either ψ_+ or ψ_- is the ground state. This conclusion is strengthened by inclusion of admixtures due to spin-orbit coupling (see below). That ψ_+ or ψ_- should lie lowest is reasonable, since the lobes of $|a\rangle$ (taken to consist mainly of $|\zeta\rangle \sim |xy\rangle$ point directly at the vacancy, which has an effective negative charge of magnitude $-2e$. In Griffith's notation [8], $|\zeta\rangle \sim yz$ and $|\eta\rangle \sim zx$ (see Figs. 3(b) and 4(b)); from electrostatic considerations, one would expect ψ_- to be the ground state if the vacancy lies along the line $x = y$ and ψ_+ if it lies along $x = -y$.

The g -shift results from admixtures to the ground state by spin-orbit coupling. If ψ_- lies lowest we calculate (to first order in perturbation theory)

$$g_x = 2.0023 - \frac{2\lambda}{E_1} - \frac{6\lambda}{E_3}$$

$$g_y = 2.0023 - \frac{2\lambda}{E_2}$$

$$g_z = 2.0023 - \frac{2\lambda}{\delta}$$

where the energy separations are defined in Fig. 4. λ is the spin-orbit coupling constant, which we take here to have the free-ion value of 154 cm^{-1} (e.g. Ref. [8]). If the positions of the two lowest states of Fig. 4 are reversed, the above equations are again obtained, but with g_x and g_y interchanged. Since the experimental assignment of these axes was arbitrary, we cannot distinguish between the two cases.

The energy gap between ψ_+ and ψ_- is found from the equation for g_z to be about 1300 cm^{-1} . If g_y for ψ_- is taken to correspond to g_y measured experimentally, we find $E_2 \approx 5500 \text{ cm}^{-1}$. The departure from octahedral symmetry is therefore large, since otherwise E_2 would have been of the order of Δ , expected to be about $20,000 \text{ cm}^{-1}$ [10]. The alternative choice of g_y gives an even bigger value of E_2 . We cannot calculate the remaining energy parameters E_1 and E_3 from the third g factor without further information; if E_3 is given the approximate value $30,000 \text{ cm}^{-1}$, then E_1 is calculated to be about 3300 cm^{-1} .

When spin-orbit coupling admixtures are included with ψ_+ or ψ_- as ground state the value predicted for A_z becomes

$$A_z = P \left\{ -\kappa + \frac{2}{7} - 2\frac{\lambda}{\delta} + \frac{3\lambda}{7} \left(\frac{1}{E_1} - \frac{1}{E_3} + \frac{1}{E_2} \right) \right\}.$$

With the values of the energy separations obtained above, this now gives a calculated value $|A_z| = 12.3 \times 10^{-4} \text{ cm}^{-1}$, in better agreement with experiment. The major correction term is that in $(\delta)^{-1}$.

It is a little surprising that a vacancy could so greatly distort the original octahedral field; it is possible that the orthorhombic splitting is enhanced by displacement of the Ti^{3+} ion towards the vacancy. Association of the Ti^{3+} with other metal ion impurities is considered improbable since these are likely to be in a high charge state (e.g. Ti^{4+} , Al^{3+}) or paramagnetic (e.g. Mn^{2+} , Fe^{3+}).

4. CONCLUSIONS

An orthorhombic spectrum ascribed to Ti^{3+} is reported; the observed departure from octahedral symmetry is large. Charge-compensation considerations suggest that the Ti^{3+} may be associated with a positive-ion vacancy in the [110] direction. From the hyperfine structure the ground state is shown to be either $2^{-1/2}(|\xi\rangle + |\eta\rangle)$ or $2^{-1/2}(|\xi\rangle - |\eta\rangle)$. The energy difference between these two states is found from the g factors to be about 1300 cm^{-1} .

An alternative explanation to distortion of the octahedral field by a cation vacancy could be provided by the Jahn-Teller theorem. Since the ground state of Ti^{3+} in an octahedral field is orbitally degenerate, the system could distort to lower its energy. Considerations of the behavior of an orbital triplet have suggested that the stable configuration would be of trigonal or tetragonal symmetry, rather than orthorhombic [11]. That this is not necessarily the case, however, has been demonstrated by recent EPR experiments on Cu^{2+} in CdF_2 [12], where the orbital triplet ground state is believed to undergo a Jahn-Teller distortion to an orthorhombic configuration.

With the available information it is not possible to distinguish between the two possible models. However, since charge compensation leads one to expect vacancy-associated titanium centers, the structure proposed in Fig. 3(b) does seem the more likely.

We note finally that we have found no evidence of a corresponding orthorhombic spectrum in a crystal of calcium oxide doped with 0.1 per cent by weight of TiO_2 .

Acknowledgements—We should like to thank S. R. P. Smith for useful discussion. Part of the work was carried out while one of us (J. J. D.) was at the Clarendon Laboratory, Oxford during the tenure of a Science Research Council Fellowship, which is gratefully acknowledged.

REFERENCES

1. WERTZ J. E., SAVILLE G. S., HALL L. and AUZINS P., *Proc. Br. ceram. Soc.* **1**, 59 (1964).

2. DAVIES J. J. and WERTZ J. E., *J. Magnetic Resonance* **1**, 500 (1969).
3. JEFFRIES C. D., *Phys. Rev.* **92**, 1262 (1953).
4. WERTZ J. E. and AUZINS P., *Phys. Rev.* **106**, 484 (1957).
5. DAVIES J. J., SMITH S. R. P. and WERTZ J. E., *Phys. Rev.* **178**, 608 (1969).
6. HENDERSON B. and WERTZ J. E., *Adv. Phys.* **17**, 749 (1968); HENDERSON B., WERTZ J. E., HALL T. P. P. and DOWSING R. D. To be published.
7. WERTZ J. E. and AUZINS P., *Phys. Rev.* **106**, 484 (1957); GRIFFITHS J. H. E. and ORTON J. W., *Proc. phys. Soc.* **73**, 948 (1959).
8. GRIFFITH J. S., *The Theory of Transition Metal Ions*. Oxford University Press (1960).
9. ABRAGAM A. and PRYCE M. H. L., *Proc. R. Soc. Lond.* **A205**, 135 (1951).
10. JØRGENSEN C. K., *Acta chem. scand.* **11**, 73 (1957).
11. A review is given by HAM F. S., *Electron Paramagnetic Resonance* (Edited by S. Geschwind). Plenum Press, New York (1970).
12. von HOENE D. C. and FEDDER R. C., *Phys. Lett.* **30A**, 1 (1969); SMITH S. R. P., Private communication.

EFFECT OF ORDERED VACANCIES ON ULTRASONIC WAVE PROPAGATION IN SOME MERCURY-INDIUM TELLURIDES

G. A. SAUNDERS and T. SEDDON

Department of Applied Physics and Electronics, The University of Durham, England

(Received 5 December 1969)

Abstract—The compounds HgTe , $\text{Hg}_5\text{In}_2\text{Te}_8$ and $\text{Hg}_3\text{In}_2\text{Te}_6$ constitute a series in which the concentration of vacancies, sited regularly on the lattice array, increases progressively from zero. To assess the effect of vacancies on the mechanical properties the propagation of 10 MHz ultrasonic waves has been studied in these compounds. The elastic constants show a regular trend through the series, namely that the stiffness decreases as the vacancy concentration increases. In particular, the reduced bulk modulus is found to be directly proportional to the number of vacancies present. Bordoni-type relaxation peaks occur in all three compounds and are consistent with dislocation motion on the $\{111\}$ and $\{110\}$ slip planes. The activation energies for kink formation and the Peierls stresses, calculated on the basis of the kink nucleation theory, show that dislocation motion becomes easier with increased vacancy concentration and takes place more readily on the $\{111\}$ slip planes.

1. INTRODUCTION

MUCH interest has been aroused in the band structure and electron transport properties of HgTe and its pseudobinary alloys with other II-VI compounds or III₂VI₃ compounds. HgTe itself is a semimetal in consequence of a small band overlap. Progressive addition of another telluride, such as CdTe or In_2Te_3 , causes the energy overlap to decrease until it goes through zero; the closer the band edges are, the smaller is the carrier effective mass and the greater is the carrier mobility. Narrow band gap alloys find use in fabrication of tunable long wavelength infrared lasers or detectors. Addition of In_2Te_3 to HgTe reduces the band gap linearly with lattice parameter a_0 until the composition 37.5 mol. % In_2Te_3 is attained [1]; the zero gap alloy has a composition corresponding to 4 mol. % In_2Te_3 . Compounds $\text{Hg}_5\text{In}_2\text{Te}_8$ and $\text{Hg}_3\text{In}_2\text{Te}_6$ are extant respectively at 37.5 mol. % In_2Te_3 and 50.0 mol. % In_2Te_3 in Hg_3Te_3 [2]. Direct energy gaps in these compounds are 0.61 and 0.78 eV respectively [3].

Although the electronic properties of these compounds have been examined extensively,

few complementary details of the lattice and mechanical properties are available. The present concern is to report the elastic and anelastic properties of $\text{Hg}_5\text{In}_2\text{Te}_8$, measured by the pulse echo technique. Results are compared and correlated with those of HgTe [4] and $\text{Hg}_3\text{In}_2\text{Te}_6$ [5]. These compounds provide an interesting series in which the zincblende structure of HgTe is modified to a defect tetrahedral structure of the same basic mould. $\text{Hg}_5\text{In}_2\text{Te}_8$ and $\text{Hg}_3\text{In}_2\text{Te}_6$ have incomplete lattices; while the formulae are stoichiometric, not every available lattice site is occupied. A vacancy can be designated $\square$. Then $\text{Hg}_5\text{In}_2\square\text{Te}_8$ has one vacancy in every eight cation sites and $\text{Hg}_3\text{In}_2\square\text{Te}_6$ one in every six cation sites. In both compounds the charges are balanced; $\text{Hg}_5\text{In}_2\square\text{Te}_8$ can be thought of as being formed by replacing 3Hg^{2+} by 2In^{3+} plus one vacancy and $\text{Hg}_3\text{In}_2\square\text{Te}_6$ similarly. Furthermore, both compounds can be produced with ordered lattices; in each case the vacancies and the mercury and indium atoms form an ordered superlattice on those sites occupied by mercury in HgTe itself. One aim of the present work has been to assess the way in which the

presence of vacant lattice sites on an ordered array affect the elastic properties of materials in general.

The presence of vacancies on a large scale should also affect the ultrasonic wave damping, in particular that associated with dislocation movement. Previously, ultrasonic wave propagation has been studied extensively in HgTe, with the object of assessing both intrinsic properties and the effects of material imperfections [6]. Dislocation damping was shown to play an important role; Bordoni-type relaxation peaks resulting from intrinsic dislocation effects were observed. Similar peaks have now been observed in $\text{Hg}_3\text{In}_2\text{Te}_6$ and $\text{Hg}_5\text{In}_2\text{Te}_8$ and are reported here. Results have been interpreted on the basis of the kink nucleation theory [7]; the activation energy for kink formation and the Peierls energy barrier to dislocation motion on the slip planes have been estimated for all three compounds. It is found that the presence of vacancies profoundly modifies not only the elastic properties but also the basic dislocation motion parameters.

2. EXPERIMENTAL DETAILS AND RESULTS

Single crystals of the compounds were grown by the Bridgman technique from elements of 99.999 per cent purity contained in evacuated (10^{-4} torr) quartz tubes. To ensure mixing and complete reaction before crystal growth and to prevent excessive build up of mercury vapour pressure, the furnace temperature was first increased slowly over several days to 750°C . A solid state, potentiometric, stepless controller employing Pt-13% Rh sensing thermocouples, controlled the temperature. A gradient of $35^\circ\text{C}/\text{cm}$ was maintained at the freezing interface. Crystals were grown from the conical tip of the tube by pulling through the temperature gradient at 1 mm/hr. Specimens cut from the main body of the boule showed no veinous or cellular structure and, as evidenced by lack of spot splitting or spreading on Laue back-reflection photographs, no mosaic structure

or strain. Any grain boundaries were revealed by an etch (one part each by volume of concentrated HCl and HNO_3 and two parts distilled water) followed by washing with concentrated HCl and then distilled water.

During this work an order-disorder transformation has been observed in $\text{Hg}_3\text{In}_2\text{Te}_6$. Further details will be discussed elsewhere. Samples quenched rapidly in liquid nitrogen after annealing at high temperatures (between 350 – 600°C) give Debye-Scherrer powder photographs which closely resemble those of HgTe and demonstrate a point group of $43m$; the lattice spacing a_0 is $6.289 \pm 0.002 \text{ \AA}$. Two interpenetrating face centred cubic lattices relatively displaced one quarter of the distance along the cube diagonal, comprise this structure; the tellurium atoms occupy one of these face centred cubic sublattices, while the mercury and indium atoms and the vacancies are disposed in disordered array on the other. Slowly cooled specimens ($\sim 3^\circ\text{C}$ per hr) and samples annealed at 300°C for about 200 hr give Debye-Scherrer photographs with superlattice lines also. The lattice spacing based on the zincblende cell is $6.290 \pm 0.001 \text{ \AA}$, which is identical to that in the disordered compound. Back reflection photographs verify the cubic nature of the ordered compound to within the experimental error of $\pm 0.5^\circ$. The calculated X-ray density ($7.05 \pm 0.01 \text{ g.cm}^{-3}$) is in reasonable agreement with that measured by Archimedes principle ($7.10 \pm 0.05 \text{ g.cm}^{-3}$). Studies reported here concern the ordered compound to allow direct comparison with ordered $\text{Hg}_3\text{In}_2\text{Te}_6$ and HgTe.

The single crystals were aligned to within $\pm 0.5^\circ$ of the [110] crystallographic axis by use of Laue back-reflection X-ray photographs. Two (110) faces were cut with a diamond wheel and lapped flat and parallel to each other to better than 0.0002 cm to avoid ultrasonic diffraction and phase sensitivity effects. Ultrasonic wave transit times were measured to an accuracy of ± 1

per cent by the single-ended, pulse-echo technique. To assist adherence of the transducers, the surfaces were lightly etched by the grain boundary etch. Resonant, gold-plated quartz transducers (fundamental frequency 10 MHz, *X*-cut for longitudinal and *Y*-cut for shear waves) were used to excite the ultrasound. The temperature range of the shear wave measurements was limited because the bonding material used (10^6 centistoke silicone fluid) was unsatisfactory above about 220°K. However the ultrasound velocities were almost temperature independent. Both velocity and attenuation were measured at a carrier frequency of 10 MHz, attenuation at higher frequencies being too high in the ternary compounds to allow satisfactory pulse-echo trains. Nevertheless, at 10 MHz numerous pulses were observed and the decay was exponential.

Measurements were taken from 77°K upwards in a cryostat described elsewhere [8]. To prevent development of a temperature gradient, the sample was immersed in a non-flammable, five component, organic mixture of 14.5% chloroform, 25.3% methylene chloride, 33.4% ethyl bromide 10.4% transdichloroethylene and 16% trichloromethylene. Temperatures were read from copper constantan thermocouples adjacent to the sample.

Ultrasound velocities v_i of longitudinal, slow and fast shear waves propagated at the [110] direction were measured. In this case

$$\begin{aligned}\rho v_1^2 &= \rho v^2 \text{ long} = (C_{11} + C_{12} + 2C_{44})/2 = C_u; \\ &\quad \mathbf{q}_1 \text{ along } [110]; \\ \rho v_2^2 &= \rho v^2 \text{ shear(1)} = C_{11}; \quad \mathbf{q}_2 \text{ along } [001]; \quad (1) \\ \rho v_3^2 &= \rho v^2 \text{ shear(2)} = (C_{11} - C_{12})/2 = C'; \\ &\quad \mathbf{q}_3 \text{ along } [1\bar{1}0];\end{aligned}$$

where ρ is the sample density and $\mathbf{q}$ is the polarisation vector. All three elastic constants C_{11} , C_{12} and C_{44} are obtainable from this

data. But the three elastic constants C_{11} , C_{44} and C' have direct physical significance and it is these that are plotted in Fig. 1. The results shown here have been obtained by a line of regression curve fit by computer to a large number of data points. Elastic constant data for all three compounds may be compared in Table 1. For completion, Table 2 gives the elastic compliance constants S_{ij} obtained by the transformation

$$S_{ij} = (-1)^{i+j} \Delta'_{ij} / \Delta' \quad (2)$$

where Δ' is the determinant of the C_{ij} terms and Δ'_{ij} is the minor of the element C_{ij} .

Figure 2 illustrates the temperature dependences of the attenuation of longitudinal and transverse waves propagated down the [110] direction in $\text{Hg}_{1-x}\text{In}_x\text{Te}$. Pronounced peaks at 109°K are observed for all three types of ultrasonic wave. In each case

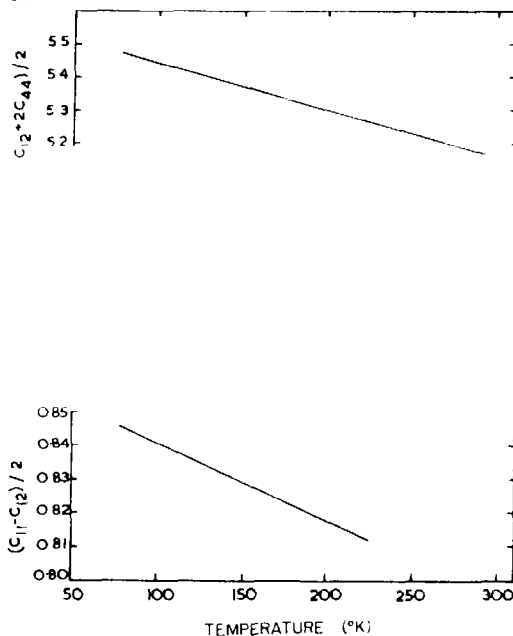


Fig. 1 The temperature dependence of the linear combinations of the elastic constants of $\text{Hg}_{1-x}\text{In}_x\text{Te}$. The lines drawn are the computed lines of regression from numerous data points in each case. The units are 10^{11} dyn cm $^{-2}$.

Table 1. Comparison between the elastic stiffness constants of $\text{Hg}_3\text{In}_2\text{Te}_6$, $\text{Hg}_5\text{In}_2\text{Te}_8$, HgTe at 77°K. Units are 10^{11} dyn cm^{-2}

Elastic constant	$\text{Hg}_3\text{In}_2\text{Te}_6$	$\text{Hg}_5\text{In}_2\text{Te}_8$ (Ref. [5])	HgTe (Ref. [4])
$(C_{11} + C_{12} + 2C_{44})/2$	5.48	6.25	7.13
$(C_{11} - C_{12})/2$	0.846	0.84	0.88
C_{44}	1.99	2.08	2.21
C_{11}	4.33	5.02	5.80
C_{12}	2.64	3.33	4.04
$(C_{11} + 2C_{12})/3$: Bulk modulus	3.20	3.89	4.62
C_{12}/C_{44} : Cauchy relation	1.33	1.60	1.83
$2C_{44}/(C_{11} - C_{12})$: Anisotropy ratio	2.36	2.48	2.51
Lattice spacing (a_0) (Å)	6.289 ± 0.401	6.33 ± 0.01	6.462 ± 0.001 Å
Density (g cm^{-3})	7.10	7.30 ± 0.01	8.081 ± 0.005
Debye temperature	$147 \pm 4^\circ\text{K}$	$142 \pm 6^\circ\text{K}$	$141 \pm 4^\circ\text{K}$

Table 2. The elastic compliance constants at 77°K in units of 10^{-11} $\text{cm}^2 \text{dyn}^{-1}$

	$\text{Hg}_3\text{In}_2\text{Te}_6$	$\text{Hg}_5\text{In}_2\text{Te}_8$	HgTe
S_{11}	0.429	0.426	0.439
S_{12}	-0.163	-0.170	-0.166
S_{44}	0.503	0.481	0.452

another peak also occurs; at 145°K for the shear wave with polarisation vector $\mathbf{q}$ along the [100] direction and at 164°K for both the other shear wave ($\mathbf{q}$ parallel to $[\bar{1}10]$) and the longitudinal wave. The temperature at which each peak occurs is the particular concern here and only the relative attenuation need be considered. The peaks can readily be separated from the background arising from intrinsic crystal damping losses and such effects as diffraction and bond losses. With this proviso, the relative attenuation losses are measured to an accuracy of better than 5 per cent.

3. DISCUSSION

Details of the propagation of ultrasonic waves in ternary compound semiconductors are sparse. The present work furnishes an insight into the effects of extremely high vacancy concentrations on both the elastic and anelastic properties through the compound series $\text{Hg}_3\text{In}_2\text{Te}_6$, $\text{Hg}_5\text{In}_2\text{Te}_8$

and HgTe . As the vacancy concentration increases, a marked decrease in crystal stiffness ensues (see Table 1). Comparison between the elastic constants of the compounds is best effected through a normalisation procedure. The elastic properties ultimately derive from interactions between the electrons and the lattice ions. Therefore Keyes[9], to compare different materials with the zincblende structure, has reduced the elastic constants to a set of dimensionless parameters by using an elastic constant C_0 equal to e^2/d^4 , where e is the electronic charge and d is the nearest neighbour atomic distance. Then the reduced bulk modulus and shear moduli are

$$\begin{aligned} B^* &= (C_{11} + 2C_{12})/3C_0 \\ C_{44}^* &= C_{44}/C_0 \\ C_s^* &= (C_{11} - C_{12})/2C_0 \end{aligned} \quad (3)$$

and the reduced average shear modulus is

$$C^* = (C_{11} - C_{12} + 3C_{44})/5C_0. \quad (3a)$$

The reduced moduli for the three compounds and ZnS are presented in Table 3. For HgTe and ZnS these reduced moduli fall directly into the range occupied by zincblende structure, II-VI compounds, namely $B^* \sim 1.1$ to 1.2 , $C_{44}^* \sim 0.6$, $C_s^* \sim 0.2$ and $C^* \sim 0.4$. HgTe itself shows no anomalous elastic behaviour[4]. But this is not so for $\text{Hg}_3\text{In}_2\text{Te}_6$

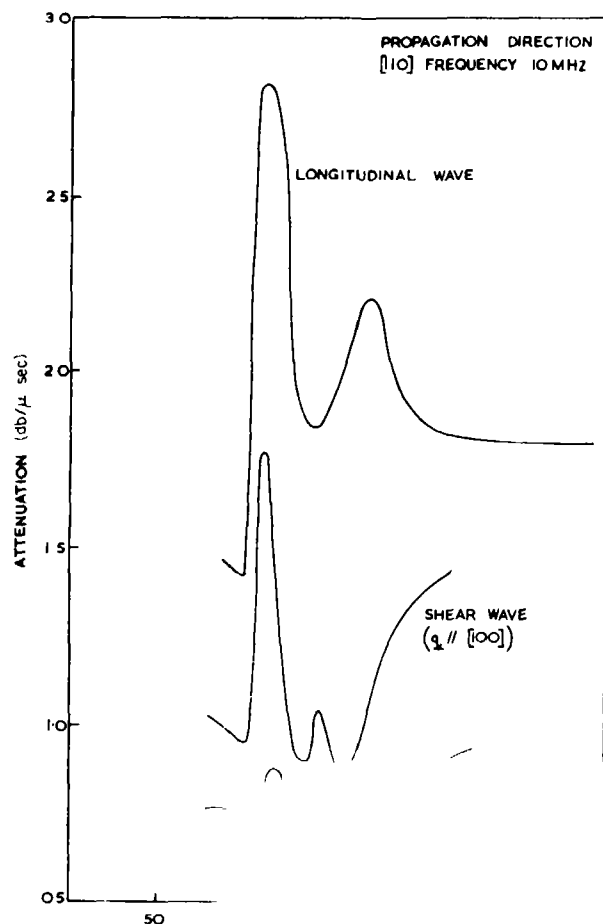


Fig. 2. The temperature dependence of the attenuation of longitudinal and transverse ultrasonic waves of frequency 10 MHz propagated down the $[110]$ direction in $\text{Hg}_3\text{In}_2\text{Te}_6$. Some substructure was observed in the 109°K peak found for attenuation of the longitudinal wave, the envelope only is shown here.

$\text{In}_2\text{□Te}_6$ and $\text{Hg}_3\text{In}_2\text{□Te}_6$. The reduced moduli, like the actual moduli, decrease smoothly through the sequence HgTe , $\text{Hg}_5\text{In}_2\text{□Te}_6$, $\text{Hg}_3\text{In}_2\text{□Te}_6$. Such a decrease in the stiffness would follow naturally from the increasing vacancy concentration. The bulk modulus $(C_{11} + 2C_{12})/3$ or its inverse the compressibility—the proportional decrease in volume of a crystal when subjected to

unit hydrostatic pressure—have direct physical significance and are the simplest properties to discuss. Like the other stiffness moduli, the bulk moduli increase through the sequence $\text{Hg}_3\text{In}_2\text{□Te}_6$, $\text{Hg}_5\text{In}_2\text{□Te}_6$, HgTe . A plot of the reduced bulk moduli B^* against the percentage of vacancies (Fig. 3) produces a fact of fundamental import: the bulk modulus is a linear function within experi-

Table 3. The reduced elastic stiffness moduli, ionicity and force constants of $\text{Hg}_3\text{In}_2\Box\text{Te}_6$, $\text{Hg}_5\text{In}_2\Box\text{Te}_8$ and HgTe . Parameters are based on the elastic constants C_{ij} measured at 77°K

	$\text{Hg}_3\text{In}_2\Box\text{Te}_6$	$\text{Hg}_5\text{In}_2\Box\text{Te}_8$	HgTe	ZnS (Ref. [9])
Reduced moduli.				
$C = 256e^2/9a_0$	4.19 ± 0.02	4.08 ± 0.04	3.76 ± 0.01	
$(C_{11} + 2C_{12})/3C_0$	0.76 ± 0.02	0.95 ± 0.03	1.23 ± 0.03	1.11
C_{11}/C_0	0.48 ± 0.01	0.51 ± 0.02	0.60 ± 0.01	0.56
$(C_{11} - C_{12})/2C_0$	0.20 ± 0.01	0.21 ± 0.02	0.24 ± 0.02	0.24
$(C_{11} - C_{12} + 3C_{44})/5C_0$	0.37 ± 0.01	0.39 ± 0.04	0.45 ± 0.02	0.43
Ionicity (e^+)	0.37 ± 0.04	0.47 ± 0.05	0.65 ± 0.05	0.65(Ref. [11])
Force constants (Born model)				
α	2.4×10^4	2.9×10^4	3.8×10^4	
β	1.9×10^4	2.4×10^4	3.2×10^4	
$4C_{11}(C_{11} - C_{12})/(C_{11} + C_{12})^2$ (Born stability condition)	0.84	0.85	0.86	

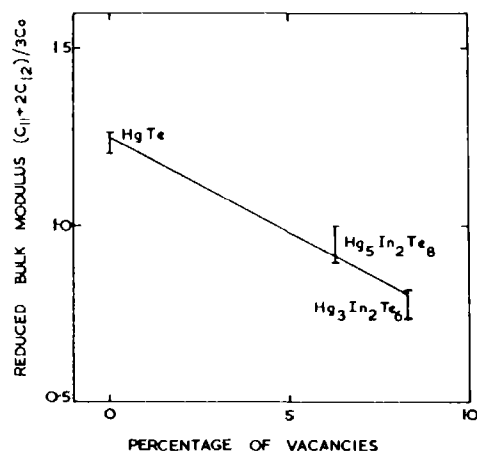


Fig. 3. The reduced bulk modulus plotted against the vacancy percentage in each compound

mental error of the number of vacancies present. Thus the change in reduced bulk modulus ΔB^+ , or its inverse the reduced compressibility ΔK^+ , can be expressed in terms of the vacancy percentage (η) by

$$\Delta B^+ = \frac{1}{\Delta K^+} = 0.053 \eta. \quad (4)$$

Each additional vacancy increases the compressibility by the same amount. This suggests a general law for the change in

compressibility due to an ordered array of vacancies.

If the line in Fig. 3 is extrapolated out to higher vacancy concentrations, the reduced bulk modulus becomes zero at 23.3 per cent vacancies, or 70% In_2Te_3 in Hg_3Te_3 . A solid with a zero bulk modulus cannot be stable and the crystal structure must change. In fact, the phase diagram[2] shows that at 71% In_2Te_3 at 650°C, the cubic phase no longer exists at all and a new phase, centred about 75% In_2Te_3 (that is $\text{HgIn}_2\Box\text{Te}_6$), occurs, which has a chalcopyrite structure.

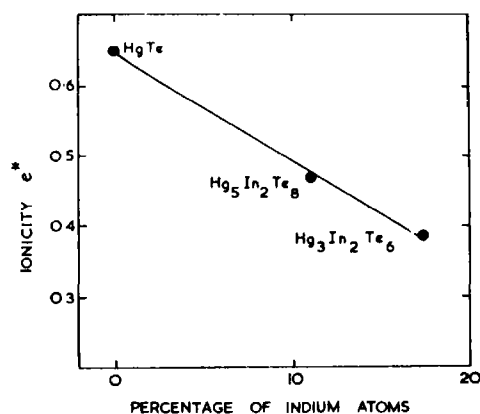


Fig. 4. The ionicity e^+ as a function of the percentage of indium atoms in each compound.

Between 54% In_2Te_3 and 71% In_2Te_3 a two phase region is extant containing both $\text{Hg}_3\text{In}_2\text{□Te}_6$ and $\text{HgIn}_2\text{□Te}_4$. It is tempting to suggest that the two phase region is stabilized because the high compressibility $\text{Hg}_3\text{In}_2\text{□Te}_6$ grains are surrounded by a matrix of $\text{HgIn}_2\text{□Te}_4$ and that when the bulk modulus of the former grains goes to zero, they can no longer be held and all the material transforms completely to the $\text{HgIn}_2\text{□Te}_4$ chalcopyrite structure. While the reduced bulk modulus shows a rapid decrease with vacancy concentration, the shear modulus changes are much less pronounced: the crystals are not unstable to shear but to the bulk dilatation.

Comparison between the interatomic binding in the different compounds can be made by reference to the two Hooke's law constants α and β , arising from radial and angular forces respectively, in Born's model and obtainable from [10]

$$\begin{aligned} C_{11} &= \frac{\alpha}{2d} \\ C_{12} &= \frac{\alpha}{2d} \left(\frac{2\beta}{\alpha} - 1 \right) \\ C_{11} &= \frac{\alpha}{2d} \left(1 - \frac{\beta^2}{\alpha^2} \right). \end{aligned} \quad (5)$$

Calculated values of α and β are given in Table 3, and demonstrate that these interatomic forces decrease through the sequence HgTe , $\text{Hg}_3\text{In}_2\text{□Te}_6$, $\text{HgIn}_2\text{□Te}_4$. This two constant model is based upon central forces and is not strictly valid here; if it were, then the Born relation

$$[4C_{11}(C_{11} - C_{12})]/(C_{11} + C_{12})^2 = 1 \quad (6)$$

should hold. This parameter is rather less than unity for each compound (see Table 3) but the deviation is not excessive and the model is tolerable.

Deviations from the central force model in these compounds arise from the mixed covalent-ionic nature of the interatomic

binding. Potter [11] has given an approximate relationship for cubic crystals between the ionicity e^+ and the ratio C_{11}/C_{12} :

$$e^+ = \left[\frac{1}{1.65} \left\{ \frac{C_{11}}{C_{12}} - 2.65 \right\} \right]^2. \quad (7)$$

While extension of Potter's work to ternary compounds must be treated cautiously, it does show (see Fig. 4) that the trend is for the ionicity to decrease linearly with replacement of mercury atoms by indium. Plausibly this arises because the polarization of the In-Te(III-VI) bonds is less than that of Hg-Te(II-VI) bonds.

The Debye temperatures θ_D of the three compounds, calculated by the graphical method of Leibfried [12], are essentially the same (see Table 1); the lattice vibration spectra are probably similar.

Now to turn to the problem of the peaks in the attenuation (Fig. 2). Peaks have also been observed in ultrasound attenuation in $\text{Hg}_3\text{In}_2\text{□Te}_6$; the authors are grateful to N.G. Pace for supplying the data on this compound, which is collected in Table 4 together with that for $\text{HgIn}_2\text{□Te}_4$.

in the close packed crystal directions. A small stress, in the present case resulting from the passage of the ultrasonic wave packet, produces a bulge in the dislocation line; kinks are formed where the dislocation line crosses from one Peierls valley to the neighbouring one. Thus, to force a dislocation over the Peierls potential barrier, an activation energy (W) is required for the formation of a kink pair. Experimental studies of the Bordoni peak constitute a practical way of determining the Peierls stress. The task remaining is to

Table 4. The dislocation motion parameters of the Seeger, Douth and Pfaff[7] theory calculated from the experimental data for the peaks in the attenuation in $\text{Hg}_2\text{In}_2\text{Te}_6$, $\text{Hg}_2\text{In}_2\text{Te}_6$, and HgTe . With the exception of the column headed 141°K under $\text{Hg}_2\text{In}_2\text{Te}_6$, peaks arising from the same type of motion are placed in horizontal rows

Ultrasonic mode Propagation direction	$\text{Hg}_2\text{In}_2\text{Te}_6$			$\text{Hg}_2\text{In}_2\text{Te}_6$			HgTe		
	$l \parallel [110]$ [110]	$T, q \parallel [110]$ [110]	$T, q \parallel [110]$ [110]	$l \parallel [110]$ [110]	$T, q \parallel [110]$ [110]	$T, q \parallel [110]$ [110]	$l \parallel [110]$ [110]	$T, q \parallel [110]$ [110]	$l \parallel [100]$ [100]
Frequency (ν_m)		10MHz		10MHz			10MHz		10MHz
Peak temperature (T_p)		109°K		175°K			204°K		218°K
Slip plane		(111)		(111)			(111)		(111)
Shear modulus (G)		$(C_{11}-C_{12}-C_{44})/3$		$(C_{11}-C_{12}-C_{44})/3$			$(C_{11}-C_{12}-C_{44})/3$		$(C_{11}-C_{12}-C_{44})/3$
Burgers' vector (b)		$a_0\sqrt{2}$		$a_0\sqrt{2}$			$a_0\sqrt{2}$		$a_0\sqrt{2}$
$F_1(r, \alpha)$		-6.51		-6.93			-6.96		-7.00
r		3.90		4.15			4.17		4.10
$F_2(r, \alpha)$		8.60		9.12			9.20		8.83
$H_A(\text{eV})$		0.018		0.031			0.037		0.038
$H(\text{eV})$		0.081		0.14			0.16		0.16
$(\sigma_p^0/G) \times 10^3$		1.4		3.7			4.8		4.8
$(\sigma_p^0) \times 10^7$		1.7		4.7			6.0		6.0
Peak temperature (T_p)		164°K		223°K			260°K		260°K
Slip plane		(110)		(110)			(110)		(110)
Shear modulus (G)		$(C_{11}-C_{12})/2$		$(C_{11}-C_{12})/2$			$(C_{11}-C_{12})/2$		$(C_{11}-C_{12})/2$
Burgers' vector (b)		$a_0\sqrt{2}$		$a_0\sqrt{2}$			$a_0\sqrt{2}$		$a_0\sqrt{2}$
$F_1(r, \alpha)$		-7.10		-7.38			-7.33		-7.33
r		4.25		4.42			4.40		4.40
$F_2(r, \alpha)$		9.4		9.81			9.78		9.78
$H_A(\text{eV})$		0.030		0.042			0.049		0.049
$H(\text{eV})$		0.133		0.19			0.22		0.22
$(\sigma_p^0/G) \times 10^3$		7.9		15.2			16.0		16.0
$(\sigma_p^0) \times 10^7$		6.7		12.8			15.0		15.0

find the fundamental parameters involved for the three compounds.

Kink pair formation in a dislocation line is a collective process, and the Arrhenius equation is not strictly applicable. A more precise treatment[7] follows from the stochastic process derivation of the kink production rate. Then the frequency ν and the activation energy W for the formation of a kink pair is given as a function of temperature by

$$\ln(\nu/Z) = F_1(r; \alpha). \quad (8)$$

The parameter Z can be approximated as [14]

$$Z = \frac{\pi^2 k}{6b^2} \left(\frac{1}{\rho G} \right)^{1/2} T_m \quad (9)$$

and can be obtained from experimental data for the temperature (T_m) at which the peak maximum occurs and the appropriate shear modulus (G) and Burgers vector (b). Hence, substitution of ν and Z into (8) gives $F_1(r; \alpha)$. This function $F_1(r; \alpha)$, given graphically by Seeger, Donth and Pfaff[7], is defined in terms of dimensionless variables r and α where

$$r = 2H_k/kT \quad (10)$$

$$\alpha = 1 - \frac{\pi}{8} \frac{\sigma}{\sigma_p^0} \quad (11)$$

Then r and hence H_k , the additional energy associated with a single kink in a dislocation line otherwise parallel to a Peierls valley, can be calculated. In the ultrasonic experiments the strains encountered are of the order of 10^{-7} ; the applied stress σ is very small compared to the Peierls stress σ_p^0 ; α in equation (11) is very close to unity. Knowledge of α and r leads directly to the activation energy (W) for kink pair formation through the relationship:

$$W = \frac{-d \ln \nu}{d(1/kT)} = kT \cdot F_2(r; \alpha) \quad (12)$$

using the graphical plots given for $F_2(r; \alpha)$ by Seeger, Donth and Pfaff[7]. Furthermore, the Peierls stress (σ_p^0) can be obtained from [14]

$$H_k = \frac{2}{\pi} \left(\frac{2}{5\pi} \right)^{1/2} \cdot G b^3 (\sigma_p^0 / G)^{1/2}. \quad (13)$$

This procedure has been followed for the three compounds studied here and the values for W , σ_p^0 and H_k are collected in Table 4.

One problem involved in the analysis is to choose the correct slip plane. The experimental data help to resolve this. In zinc blende lattices both $\{110\}$ and $\{111\}$ planes can be slip planes. The resolved shear stress component of the ultrasound waves differs on the two forms of slip plane, and the activation energies and the temperature (T_m) of the peak maximum should also be different. The experimental attenuation results are consistent with this view and, further, suggest which peaks should be assigned to a particular slip plane. Figure 5 illustrates the situation for the $\{110\}$ slip planes when ultrasound waves are propagated down the $[110]$ direction, the directions of

for these two possible dislocation motions the peak temperatures should reflect this. They do. Peaks occur at 164°K in the attenuation of both the longitudinal wave and the transverse wave with $\mathbf{q}$ parallel to the $[110]$ direction, while the peak for the other shear wave is found at 141°K. All three types of ultrasound wave give a peak in the attenuation at 109°K (see Fig. 2); this can be associated with dislocation motion on the $\{111\}$ slip planes for which the activation energies will be independent of atomic

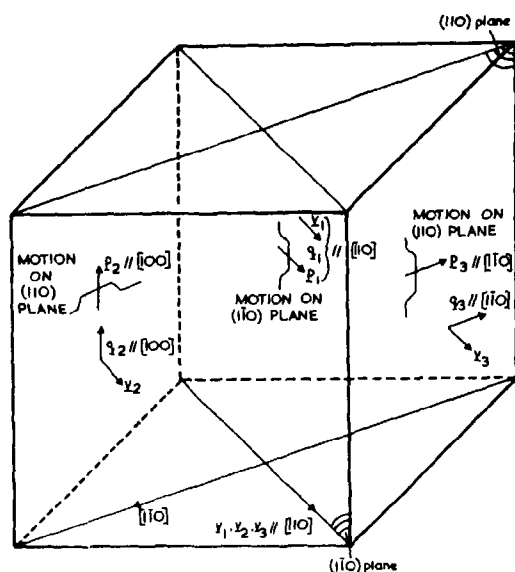


Fig. 5 To show forced dislocation motion on the $\{110\}$ planes. v_i and q_i are the ultrasonic wave velocities and polarisation vectors respectively as given in equation (1). The vectors p_i are the directions along which the dislocations are forced and the bowed lines represent the kinked dislocation lines. The Burgers vectors b_i for edge dislocations are $a_0/\sqrt{2}$ for p_1 and p_2 and a_0 for p_3 , and vice versa for pure screw dislocations.

motion direction. Pure edge dislocation motion has been assumed and the appropriate Burgers vector used. The results shown in Table 4 substantiate the basic model used for the slip planes and the dislocation motion directions. For example, for the three different ultrasound wave propagations in HgTe, the suggested $\{111\}$ plane component in each case gives the same activation energy and Peierls stress within experimental error. Direct comparison between the three materials can now be made. There are general trends

in the activation energies and Peierls stress for a given slip plane when the material is changed; both these parameters decrease through the sequence HgTe, $\text{Hg}_3\text{In}_2\text{Te}_6$, $\text{Hg}_3\text{In}_2\text{Te}_6$. This trend follows the changes in elastic properties. Thus in the most easily compressed material, namely $\text{Hg}_3\text{In}_2\text{Te}_6$ with its high vacancy concentration, dislocation motion is most easily got under way. Vacancies which are sited regularly in an ordered lattice structure do not produce localized stress and should not pin the dislocations in the same manner as ordinary vacancies. In all three compounds the activation energies and Peierls stress are lower on the $\{111\}$ planes than on the $\{110\}$; dislocation motion is easier on the $\{111\}$ planes.

Acknowledgements—The authors would like to thank Professor D. A. Wright, N. G. Pace and R. I. Cottam of the Department of Applied Physics and Electronics, University of Durham, for many useful discussions.

REFERENCES

1. WRIGHT D. A., *Br. J. appl. Phys.* **16**, 939 (1965).
2. SPENCER P. M. and RAY B., *Br. J. appl. Phys. (J. Phys. D)* **1**, 299 (1968).
3. DAHAKI S. I., *Br. J. appl. Phys.* **18**, 1340 (1967).
4. ALPER T. and SAUNDERS G. A., *J. Phys. Chem. Solids* **28**, 1637 (1967).
5. ALPER T., PACE N. G. and SAUNDERS G. A., *Br. J. appl. Phys. (J. Phys. D)* **1**, 1079 (1968).
6. ALPER T. and SAUNDERS G. A., *Phil. Mag.* **20**, 225 (1969).
7. SEEGER A., DONTH H. and PEHLI F., *Disc. Faraday Soc.* **23**, 19 (1957).
8. OKTUL O. and SAUNDERS G. A., *Proc. phys. Soc.* **91**, 156 (1967).
9. KEYES R. W., *J. appl. Phys.* **33**, 3371 (1962).
10. BORN M., *Ann. Phys.* **44**, 605 (1914).
11. POTTER R. I., *J. Phys. Chem. Solids*, **3**, 223 (1957).
12. FIBERIED G., *Handbuch der Physik* (Edited by S. Flügge), Vol. 7, p. 252. Springer, Berlin (1955).
13. SEEGER A., *Phil. Mag.* **1**, 651 (1956).
14. BORDONI P. G., NUOVA M. and VERDINI L., *Nuovo Cim.* **14**, 273 (1959).

DETERMINATION OF VALENCE AND COORDINATION OF IRON IN OXIDIC COMPOUNDS BY MEANS OF THE IRON X-RAY FLUORESCENCE EMISSION SPECTRUM

A. S. KOSTER and G. D. RIECK

Technical University, Eindhoven, The Netherlands

(Received 24 July 1969, in revised form 10 November 1969)

Abstract—The dependence of the X-ray fluorescence iron $K\beta$ spectrum of oxidic iron compounds on chemical and crystallographic structure was studied. The position of the line $K\beta_1$ is mainly determined by the valence of the iron, the position of $K\beta_{1,2}$ is also influenced by the coordination of the iron ions. The satellites occurring in the $K\beta$ spectrum give, in a qualitative way, additional information about structure.

1. INTRODUCTION

THE X-RAY emission and absorption spectra of an element are affected by the chemical bond which that element has formed. In emission, chemical influences cause the formation of additional peaks and also lead to line shifts. In absorption spectra, these influences change the position of the absorption limits and alter the appearance of the fine structure of the absorption curve, usually present at longer wavelengths than the absorption limit. At present, information about the bond type can be expected to be more easily drawn from emission spectra, since an absorption limit is more difficult to localize than the maximum of an emission band. The theoretical interpretation of the absorption edge and its fine structure may also be doubtful, our knowledge of the absorption process still being far from complete. The X-ray emission lines, on the other hand, generally arise from transitions between well defined energy states, and at present their interpretation is generally clear.

A drawback of the method, however, is that the effects involved are only small and can only be measured with a well stabilized apparatus capable of high resolution. So it is only in the last few years, that a number of contributions have been made, especially regarding elements of the third row of the

periodic system (aluminium, silicon, sulphur). For elements of the fourth row the method has been considered by Vainshtein, Ovrutskaya and Kotlyar[1], who determined the valence state of manganese in complex oxide semiconductors, and by Kolobova, Nemnonov and Agapova[2], who studied iron $K\beta$ line shifts in some oxidic compounds.

The method of Vainshtein et al. is based on the feature of being present in variable oxidation state and coordination, the method might be useful. The feature of being a non-destructive measurement in the solid state is one in common with other methods employed for the determination of spinels, like Mössbauer spectroscopy [3-5] and X-ray absorption spectroscopy [6].

2. EXPERIMENTAL

The iron spectra were recorded on a 2 kV Philips semi-automatic spectrometer PW 1220 by step scanning with intervals of $0.02^\circ 2\theta$. They were plotted by computer in order to

reduce subjective and statistical bias. Scaling was carried out by means of the integrated intensities of the $\text{Fe } K\alpha$ line. The counting time during step-scanning was so selected that the standard deviation of an intensity measurement never exceeded 1 per cent; generally it was 10 min for points in the $K\beta_5$ region and 1 min for the $K\beta_{1,3}$ region, using a chromium tube operated at 50 kV, 40 mA. Thus the spectrum was recorded in about 10 hr. No deterioration of the samples could be detected after this period. A scintillation counter with fine slits was used for recording the iron $K\beta$ spectrum, in the angular range $119\text{--}122.7^\circ 2\theta$, on a LiF analysing crystal in the 2nd order.

The position of the maximum of the $\text{Fe } K\beta_{1,3}$ band (hereafter to be called for brevity $K\beta_1$) had to be determined with the highest accuracy attainable, the shifts of $K\beta_1$ being small. Therefore, this measurement was carried out relative to a standard substance, which was chosen to be analytical grade $\alpha\text{-Fe}_2\text{O}_3$. Four samples can be accommodated in the spectrometer simultaneously. The position of the peak was roughly estimated, and then 5–6 measurements were made at both sides of the peak, manually increasing the 2θ value by 0.01° each time. In each measurement, the four samples, one of them being Fe_2O_3 , were irradiated one after another. Only the uppermost part of the curve was scanned in this way, where the intensity had not dropped below 90 per cent of the peak intensity (Fig. 1); the shape of this part of the band could be described quite adequately by a parabola, as was shown by subsequent calculations. Care was taken not to extend the region too far, the $\text{Fe } K\beta_1$ band in the compounds studied being rather asymmetric. A parabolic fit was computed by means of least squares for the 10–12 intensity values obtained for each substance, and the maximum of the parabola was calculated. By this procedure, systematic errors were avoided, while too large random errors could be detected by means of the correlation coefficient of the fit. The correlation coefficient

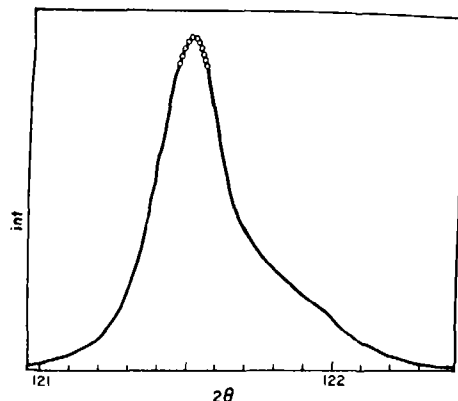


Fig. 1. The $\text{Fe } K\beta_1$ band in $\alpha\text{-Fe}_2\text{O}_3$. The points used in the parabolic fit of the top of the band are indicated. Analysing crystal LiF in the 2nd order.

generally was between 0.9998 and 1, so the parabolic fit was justified. The statistical use of the data in this way allows a relative precision of 0.001° in 2θ to be obtained, in contrast to the actual resolving power of the instrument, which is 0.01° . It was necessary of course, that the four specimen positions were reproducible, which was carefully checked.

The positions of the other peaks of the $\text{Fe } K\beta$ spectrum could not be measured with this precision. The $K\beta_5$ line is superimposed on the high energy tail of $K\beta_1$, so its apparent maximum is not the true maximum. As, again, the relative positions are the more important quantities, the position of $K\beta_5$ with respect to $K\beta_1$ was established as carefully as possible for the standard $\alpha\text{-Fe}_2\text{O}_3$, and the other $K\beta_5$ peaks were determined relative to the $K\beta_5$ peak of $\alpha\text{-Fe}_2\text{O}_3$. This was done graphically, the error being $0.005^\circ 2\theta$.

The other peaks in the $\text{Fe } K\beta$ spectrum, customarily called $K\beta'$, (to the low energy side of $K\beta_1$), $K\beta''$ (to the low energy side of $K\beta_5$) and $K\beta'''$ (to the high energy side of $K\beta_5$) were also graphically determined. Their precision is $0.02^\circ 2\theta$.

The compounds used were either commercially available materials of analytical purity grade, or preparations in our laboratory. Their purity was checked by means of Debye-

Scherrer diffraction patterns, and for some compounds a chemical analysis for the Fe^{2+} content was performed.

3. RESULTS

(a) Linearity of peak shifts

It was one of the aims of this study to relate the peak position of $\text{Fe } K\beta_1$ and/or $\text{Fe } K\beta_5$ to the valence of the iron ions present. If the peak position for Fe^{2+} is different from the peak position for Fe^{3+} , the resulting curve is a superposition of two curves, and its maximum is related to the averaged valence of iron, which may be anything between 2 and 3, although the valences of individual iron atoms can only be 2 or 3, of course. The peak position of such a compound curve was considered. It was examined experimentally as to whether a change of chemical composition changes the shape of the parabola representing the uppermost part of the emission band, since peak heights may be influenced by self-absorption or valence. All spectra were scaled by means of the integrated intensities of the $\text{Fe } K\alpha$ line, and the height of $\text{Fe } K\beta_1$ proved to be remarkably constant, the deviations being no larger than 5 per cent while the shape of the parabolas was the same in all cases. As a good approximation we can assume the parabolas representing the top of the $\text{Fe } K\beta_1$ spectra to have equal shape and magnitude. The approximation is slightly less good for the top of the $\text{Fe } K\beta_5$ profile, but the accuracy of the peak position of $\text{Fe } K\beta_5$ is also less.

The linearity of peak shift is demonstrated as follows: let the curve corresponding to valence 2 be given by

$$y_2 = -x^2 + 2bx + c. \quad (1)$$

The top of the parabola is at $x = b$. The curve corresponding to valence 3 is shifted over an amount Δb in horizontal direction with respect to curve (1); thus its representation is

$$\begin{aligned} y_3 &= -(x + \Delta b)^2 + 2b(x + \Delta b) + c \\ &= -x^2 + 2(b - \Delta b)x + d. \end{aligned} \quad (2)$$

The top of this parabola is at $x = b - \Delta b$. Let the compound curve consist of α times curve (1) and $(1 - \alpha)$ times curve (2), where $0 < \alpha < 1$; we obtain

$$\begin{aligned} y_c &= -\alpha x^2 + 2b\alpha x + c\alpha - (1 - \alpha)x^2 \\ &\quad + 2(b - \Delta b)(1 - \alpha)x + d(1 - \alpha) \\ &= -x^2 + 2x(b - \Delta b + \alpha\Delta b) + e. \end{aligned}$$

Thus the compound peak is at $b - (1 - \alpha)\Delta b$, which had to be proven.

It should be kept in mind that the addition of two parabolas from spectra essentially asymmetric like the Fe spectra under consideration, will be valid only when the uppermost regions of the curves are employed, as was stated in Section 2, and when the shifts are small in comparison to the regions used.

(b) The shift of $\text{Fe } K\beta_5$

In a former study by Koster and Mendel[7] it was shown, that for the transition metals of the iron group the shift of $K\beta_5$ is in first approximation determined by the valence of the metal ion, while the much smaller shift of $K\beta_1$

is determined by the chemical composition. As an example, the mixed oxide Fe_3O_4 being $\text{Fe}_2^{+}\text{Fe}_1^{3+}\text{O}_4$, we can assign to the iron ion an overall valence of 2.67. Thus $\alpha = 0.67$, and we calculate for the $\text{Fe } K\beta_5$ shift of Fe_3O_4 using Table 1 $(1 - 0.67) \times \Delta K\beta_5(\text{FeO}-\text{Fe}_2\text{O}_3) = 0.33 \times 0.04 = 0.013^\circ$, observed 0.01° . In the other compounds, the valence of the iron present is seen to be the main factor determining the position of $\text{Fe } K\beta_5$. In FeCr_2O_4 , where Fe^{2+} is present, the $\text{Fe } K\beta_5$ shift is 0.04° as in FeO , whereas in ZnFe_2O_4 , CdFe_2O_4 , LiFe_5O_8 , MgFe_2O_4 and $\text{BaFe}_{12}\text{O}_{19}$, where only Fe^{3+} is

Table 1. Shifts $\Delta K\beta_1 = \text{Fe}K\beta_1$ (compound) $-\text{Fe}K\beta_1(\text{Fe}_2\text{O}_3)$ and $\Delta K\beta_5 = \text{Fe}K\beta_5$ (compound) $-\text{Fe}K\beta_5(\text{Fe}_2\text{O}_3)$, expressed in degrees 2θ for the analysing crystal LiF 2nd order, and in eV. Peak positions for Fe_2O_3 are, for $K\beta_1$ 121.470° , for $K\beta_5$ 120.10°

Compound	$\Delta K\beta_1$ (2θ)	$\Delta K\beta_1$ (eV)	$\Delta K\beta_5$ (2θ)	$\Delta K\beta_5$ (eV)
Fe_2O_3	0	0	0	0
Fe_3O_4	+0.0035	+0.12	+0.01	+0.4
FeO	+0.006	+0.21	+0.04	+1.4
ZnFe_2O_4	-0.005	-0.17	+0.00	+0.0
CdFe_2O_4	-0.004	-0.14	+0.00	+0.0
LiFe_5O_8	+0.000	+0.00	+0.00	+0.0
LiFe_2O_4	+0.003	+0.10	+0.01	+0.4
MgFe_2O_4 (1300°)	-0.002	-0.07	+0.00	+0.0
MgFe_2O_4 (660°)	-0.001	-0.03	+0.00	+0.0
MgFe_2O_4 (360°)	-0.001	-0.03	+0.00	+0.0
GeFe_2O_4	-0.001	-0.03	+0.03	+1.1
FeCr_2O_4	+0.020	+0.69	+0.04	+1.4
$\text{BaFe}_{12}\text{O}_{19}$	-0.005	-0.17	+0.01	+0.4
error	± 0.001	± 0.03	± 0.005	+0.2

present, the $\text{Fe}K\beta_5$ peak position is the same as in Fe_2O_3 . In partly reduced LiFe_5O_8 (denoted in Table 1 by LiFe_2O_4), where the valence of iron was chemically determined as 2.71, the shift was $+0.01^\circ$ (calculated $+0.012^\circ$). In GeFe_2O_4 the valence of iron was 2.40; the shift was $+0.03^\circ$ (calculated 0.024°).

We can thus conclude that the shift of $\text{Fe}K\beta_5$ is a measure of the valence of iron; the accuracy, however, is rather low, the valence determination being accurate to about 15 per cent.

(c) The shift of $\text{Fe}K\beta_1$

The $\text{Fe}K\beta_1$ shifts are more complicated. It is seen in Table 1, that $\text{Fe}K\beta_1$ does not shift linearly with the mean valence; for Fe_3O_4 we calculate $0.33 \times \Delta K\beta_1(\text{FeO}-\text{Fe}_2\text{O}_3) = 0.33 \times 0.006^\circ = 0.002^\circ$, while the observed value of 0.0035° is significantly larger. Thus the oxygen coordination around the Fe ion influences the shift. Especially important are the octahedral and tetrahedral configuration, as found in spinels $A^{\text{tet}}[B_2^{\text{oct}}]\text{O}_4$. The substances were so chosen as to represent several

configurations while leaving no doubt about the valence of the iron.

Experiments in the soft X-ray region, for instance by Holliday [10], indicate that valence, far more than coordination or crystal structure, determine emission band-shift. This is especially true for the transitions where valence electrons are involved, as was shown by our own $\text{Fe}K\beta_5$ measurements. In other transitions, however, the influence of valence has decreased; the effects due to local structure have become relatively more important, and thus detectable, thanks to the high accuracy of the measurements.

In the first place, it was postulated, that only the oxygen coordination and the valence of iron would influence the peak position. To check this, the $\text{Fe}K\beta_1$ positions of $\text{Zn}[\text{Fe}_2]\text{O}_4$ and $\text{Cd}[\text{Fe}_2]\text{O}_4$ were compared; they were the same within experimental error, and so it was assumed that the position of the peak was independent of the other cation(s).

Octahedral iron. In ZnFe_2O_4 and CdFe_2O_4 there exists octahedral Fe^{3+} , while in FeO the Fe^{2+} ion also occupies octahedral sites. In Table 1 we see that the shifts are -0.005° for Fe^{3+} and 0.006° for Fe^{2+} , always with respect to $\alpha\text{-Fe}_2\text{O}_3$. The compound $\text{BaFe}_{12}\text{O}_{19}$ has not the spinel structure, but is hexagonal; this structure can be described as consisting mostly of octahedrally surrounded Fe^{3+} ions, and thus we would expect a shift value of about -0.005° ; the observed value is -0.005° .

Tetrahedral iron. A value x for the tetrahedral Fe^{3+} shift is obtained by means of Fe_3O_4 , in spinel notation $\text{Fe}^{3+}[\text{Fe}^{2+}\text{Fe}^{3+}]\text{O}_4$. Assuming additive peak shifts, the peaks over the range where shifts occur being parabolic, we have $[x + (\text{octahedral } \text{Fe}^{2+} \text{ shift}) + \text{octahedral } \text{Fe}^{3+} \text{ shift}]/3 = (x + 0.006 - 0.005)/3 = 0.0035$ and thus the tetrahedral Fe^{3+} shift x is $+0.009^\circ$. With this value we can compute the $\text{Fe}K\beta_1$ shift for LiFe_5O_8 , in spinel notation $\text{Fe}_2^{3+}[\text{LiFe}_3^{3+}]\text{O}_8$; calculated $(0.009 \times 2 - 0.005 \times 3)/5 = 0.0006^\circ$, in good agreement with the experimental value $+0.000^\circ$.

If we assume that the shift between tetra-

hedral Fe^{3+} and Fe^{2+} is 0.011° , just as the shift between octahedral Fe^{3+} and Fe^{2+} , we expect for tetrahedral Fe^{2+} a shift of $+0.020^\circ$. This value is indeed observed in $\text{Fe}[\text{Cr}_2]\text{O}_4$. We may conclude that the shifts with respect to $\alpha\text{-Fe}_2\text{O}_3$ are $+0.009^\circ$ for Fe^{3+} and $+0.020^\circ$ for Fe^{2+} .

Determining the coordination in some spinels. After determining the valence of the iron, we can employ the $\text{Fe } K\beta_1$ shift for an indication of the coordination. In $\alpha\text{-Fe}_2\text{O}_3$, there exists a slightly distorted hexagonal close-packing of oxygen ions; three $\text{Fe}-\text{O}$ bonds are substantially larger than the other three (2.06 resp. 1.91 Å). It stands to reason therefore, that the $\text{Fe } K\beta_1$ shift (0 per definition) is somewhere between -0.005° and $+0.009^\circ$, and rather more in the neighbourhood of the first, octahedral Fe^{3+} value. It would be difficult to calculate the value exactly, the figures given being derived from spinel data.

The expected $\text{Fe } K\beta_1$ shift in LiFe_xO_8 (mean Fe valence 2.71) with respect to LiFe_5O_8 (Fe valence 3) is $(1-0.71) \times 0.011 = +0.003^\circ$, observed value 0.003° .

The magnesium iron spinels are known to be partially inverse. The amount of inversion depends on the temperature at which the spinel is heated and whence it is quenched (Allen[8]). The products heated at 1300 and 660°C and 360°C are reported to be inverse

for 63, 75 and 85 per cent respectively. In these cases we calculate the shifts as follows:

$$\text{MgFe}_2\text{O}_4 (1300^\circ): 0.315 \times 0.009 + 0.685$$

$$\times -0.005 = -0.001^\circ; \text{observed } -0.002^\circ$$

$$\text{MgFe}_2\text{O}_4 (660^\circ): 0.375 \times 0.009 + 0.625$$

$$\times -0.005 = +0.000^\circ; \text{observed } -0.001^\circ$$

$$\text{MgFe}_2\text{O}_4 (360^\circ): 0.425 \times 0.009 + 0.575$$

$$\times -0.005 = +0.001^\circ; \text{observed } -0.001^\circ.$$

It follows that the findings of Allen are generally in agreement with ours. A shift of 0.001° means that a compound is more inverse for 10 per cent.

According to Durif-Varambon, Bertaut and Pauthenet[9], the spinel notation of GeFe_2O_4 is $\text{Ge}[\text{Fe}_2]\text{O}_4$. From the $\text{Fe } K\beta_5$ shift and the chemical analysis it follows that the iron is for 60 per cent present as Fe^{2+} . Assuming all Fe to be in the octahedral sites, the $K\beta_1$ shift should be $0.60 \times 0.11 - 0.005 = +0.001^\circ$; the observed value is -0.001° , which is the same, experimental errors being taken into consideration.

Table 2. Relative positions and peculiarities

Compound	$\Delta(K\beta_1 - K\beta')$ (eV)	$I(K\beta')$ $I(K\beta_1)$	$\Delta(K\beta_5 - K\beta)$ (eV)	$I(K\beta)$ $I(K\beta_5)$	$\Delta(K\beta_5 - K\beta')$ (eV)	$I(K\beta_5)$
Fe_2O_3	14.3	0.071	13.8	0.18	13.6	0.20
Fe_3O_4	13.8	0.074	14.2	0.16	(vague)	0.03
FeO	13.4	0.063	14.4	0.17	not observed	
ZnFe_2O_4	14.4	0.077	14.1	0.15	13.4	0.22
CdFe_2O_4	14.4	0.076	14.1	0.15	13.4	0.22
LiFe_5O_8	14.0	0.073	14.1	0.15	13.0	0.15
LiFe_xO_8	13.8	0.068	14.2	0.18	(vague)	0.03
$\text{MgFe}_2\text{O}_4 (1300^\circ)$	14.1	0.074	14.1	0.20	12.4	0.16
$\text{MgFe}_2\text{O}_4 (660^\circ)$	14.2	0.073	14.4	0.20	12.7	0.20
$\text{MgFe}_2\text{O}_4 (360^\circ)$	14.4	0.068	14.4	0.21	12.4	0.17
GeFe_2O_4	13.8	0.071	14.1	0.16	(vague)	0.03
FeCr_2O_4	14.4	0.074	14.8	0.15	15.8	0.18
$\text{BaFe}_{12}\text{O}_{19}$	14.8	0.077	14.1	0.14	16.4	0.22
error	± 0.3	± 0.003	± 0.5	± 0.03	± 0.5	± 0.03

tail of $K\beta_1$ or $K\beta_5$. Consequently the error both in position and intensity is rather large and the use of these lines for analytical purposes limited. Yet some interesting features may be pointed out.

The origin of these lines is discussed by Koster and Mendel [7]. The satellite $K\beta'$ is explained by the promotion to the conduction band of unpaired 3d electrons not forming part of the chemical bond. The energy for this process is supplied by the $K\beta_1$ quanta, which are accordingly decreased in energy. All of the compounds dealt with have semiconductor character, and the energy differences between $K\beta_1$ and $K\beta'$ is related to the position of the conduction band. Thus it can be explained that there is no obvious relation between structure of the compound and the energy separation $\Delta(K\beta_1 - K\beta')$; it is to be noted, that this separation is larger for compounds with large d.c. resistivity at room temperature like $\text{BaFe}_{12}\text{O}_{19}$ and Fe_2O_3 than for compounds of lower resistivity, like Fe_3O_4 and FeO . Since the number of unpaired 3d electrons to be promoted is 5 for Fe^{3+} and 4 for Fe^{2+} , the ratio of the $K\beta'$ intensities should be about 0.8 for Fe^{2+} and Fe^{3+} containing substances; the mean relative intensity observed for Fe^{3+} is 0.075, the relative intensity for FeO is 0.063, thus this ratio is experimentally found as 0.84.

The line $K\beta''$ is due to the cross-over transition of an oxygen 2s electron to an iron 1s vacancy; since $K\beta_5$ is mainly determined by the transition of an oxygen 2p electron to an iron 1s vacancy, we may expect that the separation between $K\beta_5$ and $K\beta''$ is nearly constant, being the separation between the oxygen $L_{2,3}$ and the oxygen $L_{2,III}$ level. This is indeed the case; furthermore, the relative intensity is also rather constant.

The origin of $K\beta'''$ is ascribed to the transition of an electron in the conduction band to an iron 1s vacancy and it is seen that this line is of rather variable position and intensity. It is significant that this line is not or only vaguely seen in compounds of relatively low resistivity

like Fe_3O_4 and FeO ; there is a relation between the $K\beta'$ and $K\beta'''$ lines and the conductivity, which is the subject of further study.

4. CONCLUSIONS

(1) The valence of iron in oxidic compounds can be deduced from the position of the $\text{Fe } K\beta_5$ peak, with an accuracy of about 15 per cent.

(2) The $\text{Fe } K\beta_1$ peak position contains information about the valence and the coordination of iron; in spinels, the following scheme gives line shifts with respect to $\alpha\text{-Fe}_2\text{O}_3$:

	Degrees 2θ for 1st 2nd order (eV)	
octahedral Fe^{3+}	-0.005	-0.2
octahedral Fe^{2+}	+0.006	+0.2
tetrahedral Fe^{3+}	+0.009	+0.3
tetrahedral Fe^{2+}	+0.020	+0.7
accuracy	0.001-0.002	0.05

(3) The lines $K\beta'$, $K\beta''$ and $K\beta'''$ can hardly be used for quantitative solid-state analysis due to their low precision, but contain important qualitative information about structure and resistivity.

Acknowledgement We are grateful to Mrs. T. C. van Veen-Houtman for her help in this investigation.

REFERENCES

1. VAINSHTEIN F. F., OVRUISKAYA R. M. and KOTLYAR B. I., *Fiz. tverd. Tela* **7**, 2120 (1965).
2. KOLOBOVA K. M., NEMONOV S. A. and AGAPOVA E. V., *Fiz. tverd. Tela* **10**, 729 (1968).
3. EDWARDS P. R. and JOHNSON C. F., *J. chem. Phys.* **49**, 211 (1968).
4. EIBSCHULTZ M. and GANIEL M., *Solid State Commun.* **6**, 755 (1968).
5. YAGNIK C. M. and MATHUR H. B., *Proc. phys. Soc. C Ser 2*, **1**, 469 (1968).
6. MANDE C., KUI KARNI D. K. and CHETAL A. R., *J. Phys. D Ser 2*, **2**, 635 (1969).
7. KOSTER A. S. and MENDEL H., *J. Phys. Chem. Solids* **31**, 2511 (1970).
8. ALLEN W. C., *J. Am. Ceram. Soc.* **49**, 257 (1966).
9. DURIF-VARAMBON A., BERTAUT E. F. and PAUTHENET R., *Annls Chim.* **1**, 525 (1956).
10. HOLIDAY J. E., *Soft X-Ray Band Spectra* (Edited by D. J. Fabian), p. 127. Academic Press, New York (1968).

X-RAY $K\beta$ EMISSION SPECTRA AND ENERGY LEVELS OF COMPOUNDS OF 3D- TRANSITION METALS—I OXIDES

A. S. KOSTER

Technical University, Eindhoven, The Netherlands

and

H. MENDEL*

Unilever Research Laboratory, Vlaardingen, The Netherlands

(Received 14 October 1969)

Abstract—The $K\beta$ emission spectra of calcium, titanium, chromium, manganese and iron and oxide compounds of these elements were investigated by means of the fluorescent method. The origin of the five main $K\beta$ lines is discussed, their wavelengths are given and used to construct composite energy schemes. The dependence of the level positions on the chemical bond is discussed.

1. INTRODUCTION

It has been shown by Ershov and Lukirskii [1] on SiO_2 , by Fomichev [2] on Al_2O_3 and by Mendel and Koster [3] on NaCl , NaOH , MgO , MgF_2 , Al_2O_3 , SiO_2 and SiC , that the energies involved in electron transitions in these compounds, when excited by means of X-rays or electrons, can be used to construct a composite energy diagram. This diagram consists of series of energy levels that belong to the various constituting atoms or ions and it represents the energetic state of the compound. During emission of X-ray quanta transitions are possible not only between levels of the same species, but cross-over transitions can also occur. The zero level of this scheme can be chosen arbitrarily, for instance [1] at the edge of the conduction band, but then it should be remembered, that the position of the conduction band with respect to the Fermi level is different for different materials. It is also possible [2] to deduce an absolute scale for the scheme from X-ray absorption measurements and measurements of electron affinities. In our former [3] and in the present study we have chiefly made use of photo electron data as given by

Siegbahn and coworkers [4-7]. As the energy levels are closely connected with the type of chemical bond, their evaluation is important from a physical and chemical point of view, and it may be expected that X-ray spectra can offer help to obtain information concerning the charge and coordination of the ions and the covalency of the bond. The main difficulty is

on chemical influences.

In the present paper, results are given for calcium, titanium, chromium, manganese and iron. Many data concerning these elements are available in the literature, but they still lack a common theoretical basis. The $K\beta$ spectra occur in the region 3-1.7 Å, which can conveniently be explored by means of a commercially available spectrograph. Calcium is not a transition metal in the strict sense of the word, but was included because the structure of the outer energy bands is not basically different from that of the transi-

*Present address: Department for Organic Chemistry, University, Ibadan, Nigeria

tion metals, the sd configuration being close to the ground state configuration s^2 . From cobalt onwards the $K\beta$ wavelengths become so short, that shifts and satellite lines are hard to detect reliably due to the limited resolving power of our apparatus. Cobalt, nickel and copper were included in our experiments, and the results did fit the notions set out in this paper; the precision being substantially lower, however, than in the case of the other elements, we did not use this information in explaining the $K\beta$ spectra. For these elements, the L lines should be used preferably.

2. EXPERIMENTAL

All chemicals were of the purest quality commercially available and checked by means of Debye-Scherrer photographs. Calcium metal was embedded in mounting resin, polished on a dry disk and placed rapidly into the vacuum chamber of the spectrograph. The amount of oxide on its surface can be assumed to have been very small. Lithium permanganate and iron (II) oxide not being commercially available were prepared in our laboratory.

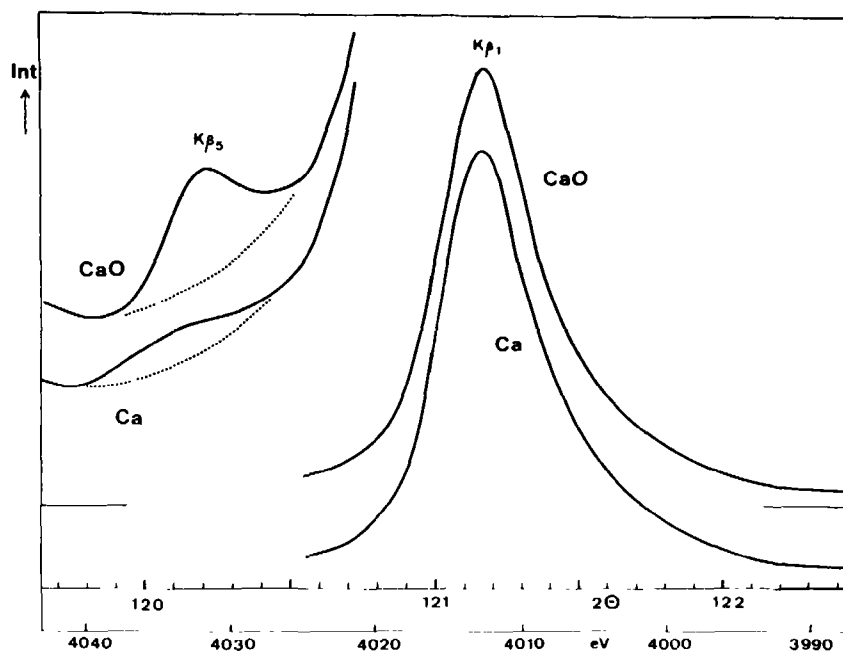
The spectra were recorded on a 2 kW

Philips semi-automatic spectrometer PW 1220 by step scanning and printing out. They were plotted by computer in order to reduce subjective and statistical bias. Scaling was carried out by means of the integrated intensities of the $K\alpha$ line. The counting time during step-scanning was so selected that the standard deviation of an intensity measurement never exceeded 1 per cent. The spectra are shown in Figs. 1-5; as the $K\beta_5$ band is much weaker than the $K\beta_{1,3}$ band it is plotted on an enlarged scale.

Accurate peak positions of $K\beta_{1,3}$ were obtained by measuring with respect to substances whose $K\beta_{1,3}$ wavelength may be considered as reliably known[8]; these were: calcium oxide, 3.0897 Å; metallic titanium, 2.5139 Å; metallic chromium, 2.0849 Å; metallic manganese, 1.9102 Å; metallic iron, 1.7566 Å. The peak positions of the other lines were measured with respect to the $K\beta_{1,3}$ line. Peak positions of the five main lines of the $K\beta$ spectrum are given in Table 1; by $K\beta_1$ we denote the doublet $K\beta_{1,3}$, by $K\beta'$ the peak to the low energy side of $K\beta_1$, by $K\beta''$ the peak to the low energy side of $K\beta_5$, by $K\beta'''$ the peak to the high energy side of

Table 1. Peak positions in degrees 2θ and in eV

	$K\beta'''$	$K\beta_5$	$K\beta''$	$K\beta_1$	$K\beta'$	$K\beta'''$	$K\beta_5$	$K\beta''$	$K\beta_1$	$K\beta'$
Ca		120.10		121.15			4033.7		4012.7	
CaO		120.20		121.15			4031.5		4012.7	
Ti		134.20		135.93			4962.7		4931.8	
TiO ₂		134.24	135.08	135.94			4962.0	4946.8	4931.6	
Cr		142.45		144.77			5986.2		5946.5	
Cr ₂ O ₃	141.67	142.59	143.35	144.75	145.72	6000.2	5983.8	5969.9	5946.9	5931.1
CrO ₃		142.38	143.26	144.83			5987.5	5972.0	5945.5	
Mn		140.87		143.15			6535.3		6490.7	
MnO		140.97		143.09	143.95		6533.2		6491.8	6475.7
MnO ₂	140.16	140.90	141.58	143.14	143.94	6549.8	6534.7	6521.0	6490.9	6475.9
MnO ₃		140.76	141.48	143.20			6537.5	6523.0	6489.7	
Fe		120.06		121.49	121.75		7108.4		7058.2	7049.2
FeO		120.13	120.54	121.48	121.87		7105.9	7091.5	7058.5	7045.1
Fe ₂ O ₃	119.70	120.11	120.52	121.47	121.88	7121.4	7106.6	7092.2	7058.8	7044.8
Fe ₂ O ₄	119.72	120.10	120.49	121.47	121.89	7120.6	7107.0	7093.1	7058.9	7044.6

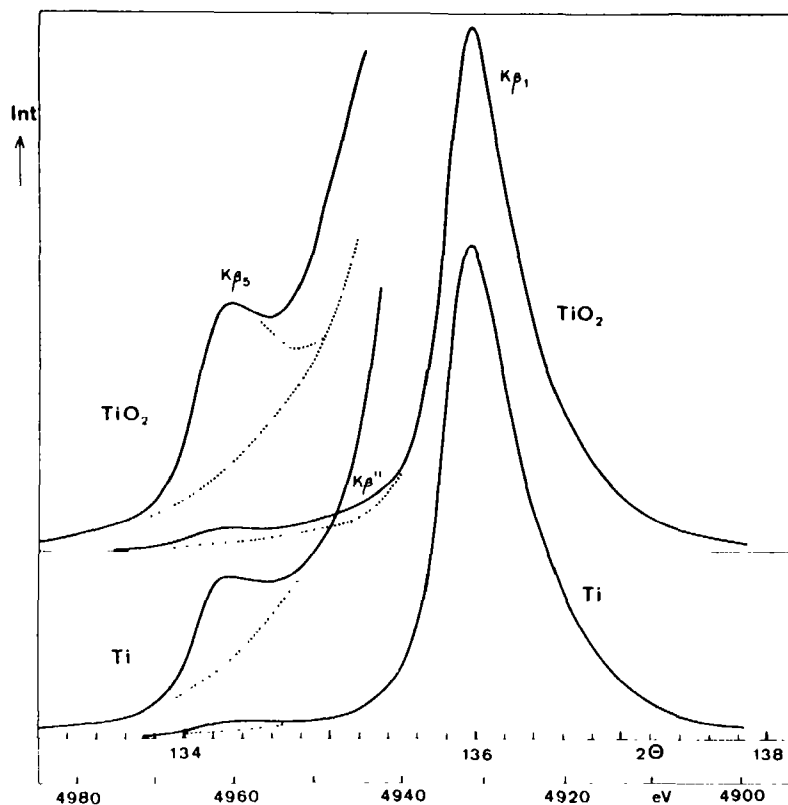
Fig. 1. $K\beta$ spectra of Ca and CaO

$K\beta_5$. The estimated error in $K\beta_1$ is 0.2 eV, in the other lines 0.4–0.6 eV. The analytical crystals were for Ca, ADP 3rd order ($d = 5.321 \text{ \AA}$); for Ti, topaz 1st order ($d = 1.356 \text{ \AA}$); for Cr, PET 4th order ($d = 4.375 \text{ \AA}$); for Mn and Fe, LiF 2nd order ($d = 2.01335 \text{ \AA}$).

3. ORIGIN OF THE $K\beta$ LINES

The $K\beta_1$ line results from a $3p-1s$ transition. As the $M_{II,III}$ and K levels containing the $3p$ and $1s$ electrons are completely filled, the shifts in $K\beta_1$ allow us to draw a general conclusion as to the shifts of these levels when increasing the valence of the metal ion or changing the covalent character of the chemical bond. In the iron oxides, which have about the same covalent/ionic character, we notice a shift of $K\beta_1$ toward higher eV values when we increase the valence of iron. This means that the $M_{II,III}$ and the K level move away from each other, and as the removal of an outer electron can only increase

the covalency of the metal-oxygen bond, experimentally found. In the manganese compounds we notice a $K\beta_1$ shift to lower eV values when we compare MnO_4^- (formally containing Mn^{7+}) with MnO_2 (Mn^{4+}) and MnO (Mn^{2+}). The same effect can be observed in the chromium compounds. It is generally recognized[10] that the bonds in the permanganate ion and in the chromate ion or chromium trioxide are mainly covalent in character, so we conclude that upon increasing the covalency of the metal-oxygen bond, the $M_{II,III}$ and K levels shift toward one another, which can only mean that the $M_{II,III}$ level

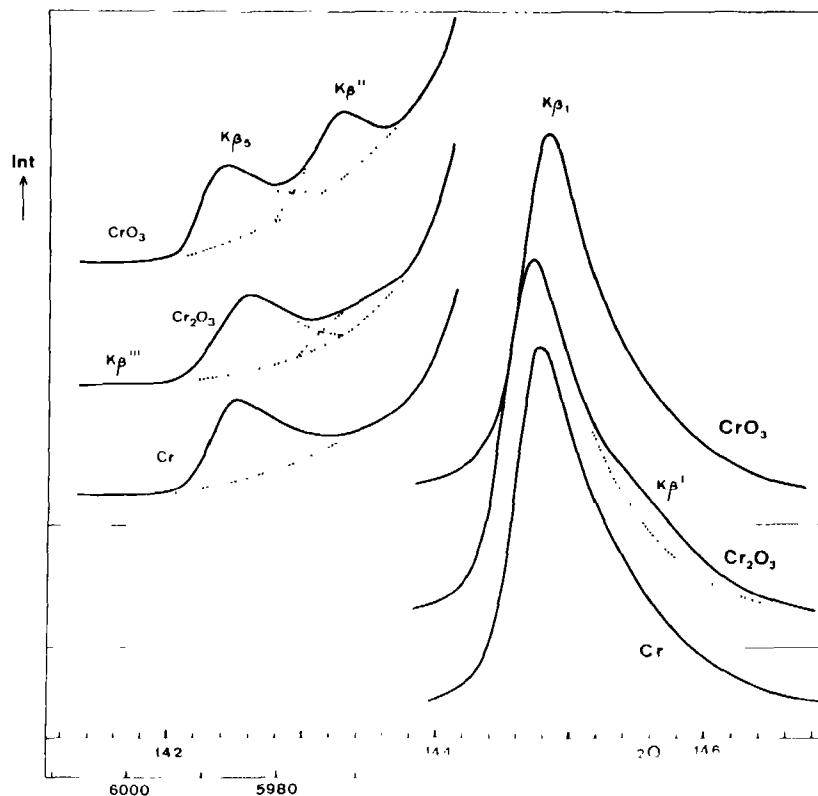
Fig. 2. $K\beta$ spectra of Ti and TiO_2 .

changes more strongly to higher values than the K level. From a chemical point of view, this is very plausible; we may assume, that the K level changes but little.

The same arguments for level shifts hold for the energy levels in oxygen, but acting in opposite direction. As oxygen is formally present as O^{2-} ions in all compounds investigated, we may assume that shifts of the K level due to change in valence are at most 1–2 eV; in our former paper[3] it was found that the binding energy of O $1s$ electrons is 532–534 eV when the residual charge is -1.8 to -0.9 electron units respectively. The oxygen $L_{II,III}$ level also changes somewhat to higher absolute value, so the resulting shift in $K\alpha$ wavelength is small. Furthermore we

may expect a shift due to change in ionic/covalent character. As a matter of fact, Fischer[11] found in a large number of oxides always about the same oxygen $K\alpha$ wavelength, corresponding to an energy of 525 ± 1 eV. He did not measure MnO_2 and CrO_3 , however; from our observations it can be inferred, that in these compounds the separation between the oxygen $L_{II,III}$ and L_I levels is increased by about 1 eV. This is in agreement with the fact, that the covalency of the bond is increased.

The $K\beta_5$ line of the pure metal results from the $3d,4s-1s$ transition, the overlapping $M_{IV,V}$ and N_I levels being spread out into valence and conduction band. In the compounds, two cases must be considered; when all valence electrons are used in bond forma-

Fig. 3 $K\beta$.

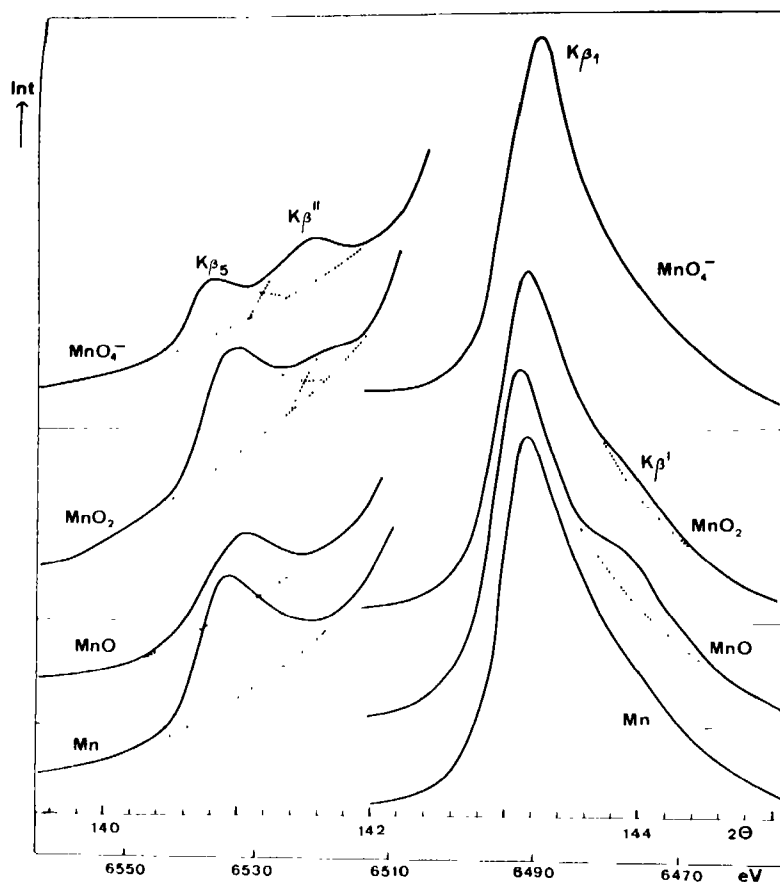
tion, the $K\beta_1$ line arises from the transition between the level mainly characterized by the $2p$ wave functions of oxygen and the $K\beta$ level of the metal, as is demonstrated by the results for MnO_2 and CrO_3 . When on the other hand there are extra $3d$ electrons, as in the case of the iron compounds, the level of the $3d$ electrons of the metal and the level of the $2p$ electrons of oxygen have about the same position in the valence band, and the transition might be called a $3d(\text{metal})$, $2p(\text{oxygen})$ – $1s(\text{metal})$ transition.

As regards the so-called satellite lines $K\beta'$, $K\beta''$, and $K\beta'''$, it has already been recognized[12–14] that the $K\beta''$ line to the low energy side of $K\beta_3$ arises from the cross-over transition of the $2s$ valence electron of

difference between $K\beta_1$ and $K\beta_3$.

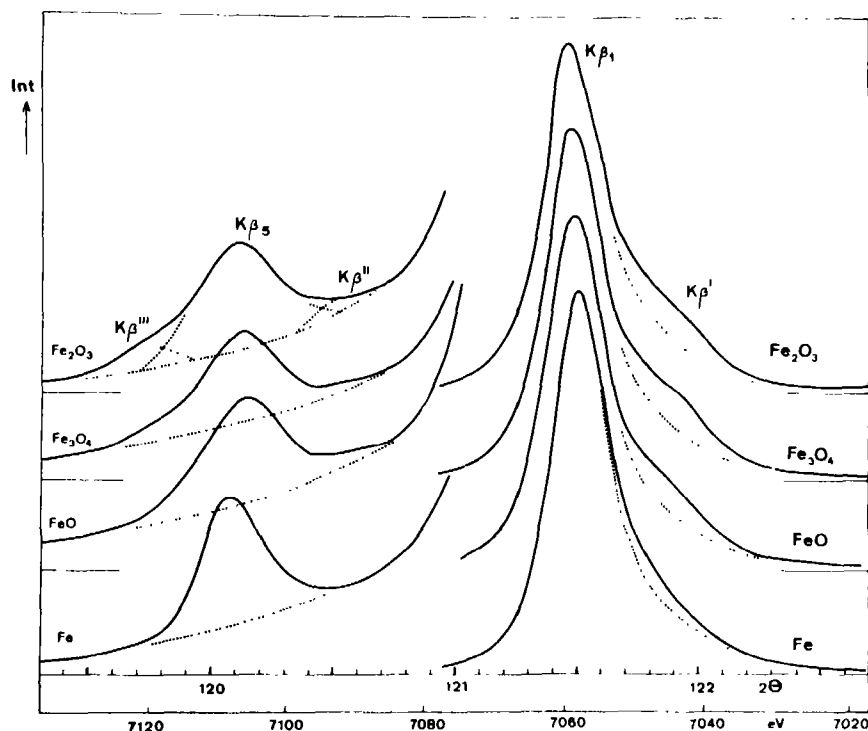
remain constant in first approximation. It is immediately seen in the recording of the spectra, that the intensity of $K\beta''$ increases with increasing amount of coordinated oxygen. This satellite occurs also in oxides in the previous row of the periodic table, for instance in Al_2O_3 [2], SiO_2 [1], P_2O_5 [15], as a low energy satellite of $K\beta$, in tables it is generally called $K\beta'$, but actually corresponds to $K\beta''$ presently discussed.

The line $K\beta'$ only appears when there are partially occupied $3d$ orbitals present in the

Fig. 4. $K\beta$ spectra of Mn and Mn oxides.

compounds; while it is visible in MnO , MnO_2 and Cr_2O_3 , it disappears in MnO_4^{2-} and CrO_3 where the $3d$ electrons are all engaged in bonding. In Fe_2O_3 and MnO with 5 holes in the $3d$ orbitals, this line shows up most strongly. As this is a line to the low energy side of $K\beta_1$, its existence could be due to a splitting of the $M_{II,III}$ level due to chemical interactions, but its large distance to $K\beta_1$ makes this assumption most unlikely. Splitting of levels due to spin-orbital interaction, giving rise to the doublet $K\beta_{1,3}$, is also impossible, this splitting being at most 1–3 eV. Men'shikov and Nemnonov[16, 17] ascribe the formation of $K\beta'$ to the exchange interaction between

the electrons of the open $3d$ shell and those of the inner shells; they note a certain linear dependency of the energy gap between $K\beta_1$ and $K\beta'$ on the atomic number for the elements Mg to Cl and Ca to Ge. Their interpretation of $K\beta'$ for the elements Mg to Cl is incorrect, however, $K\beta'$ being in reality $K\beta''$ as is explained above. The dependence for the other elements was not found in our experiments. The only regularity in our spectra was noted for the intensity of $K\beta'$, which is roughly proportional to the number of $3d$ electrons with uncompensated spins. The formation of $K\beta'$ is thought to be due to promotion of $3d$ electrons to the conduction

Fig. 5 $K\beta$ spectra

band, these substances all having semiconductor character; the energy for this transition is supplied by the self-absorption of a quantum, whose energy is accordingly decreased by the same amount. Evidence for this explanation is the fact, found by Vainshtein *et al.*[13] and by ourselves, that the integrated intensity of the $K\beta_1\beta'$ band remains constant in a series of compounds.

The $K\beta'''$ line is observed rather clearly in iron oxides on the high energy side of $K\beta_5$. Blokhin[18] explains this line by the double transition $2p3d-2p1s$. While this explanation is possible, attention should be drawn to the fact that there is a marked correspondence between the intensity of $K\beta'$ and $K\beta'''$, not only in the spectra presented in this paper, but also in those to be published in part II of this study. It is not clear, why double ionisa-

electrons to reduce the lifetime of an atom in the double ionisation state can not be valid, since nonconducting covalent iron compounds also miss this $K\beta'''$ line. Furthermore, it has been found[20] that multiple ionisation occurs mainly in primary excitation; the intensity of short wavelength satellites with the secondary method of excitation is very small compared to the intensity with electron excitation. The formation of $K\beta'''$ is thought to be due to the transition of an electron brought into the conduction band to the K level. Experimentally this fits very well.

In the above a general outline was given of the formation of the five principal lines of the $K\beta$ spectrum. It follows that it is not proper to divide these lines in diagram lines and non-diagram lines or satellites; all of them are of equal interest and fit into a diagram, which, however, for compounds is somewhat more complicated. Very probably the number is not restricted to five, since weaker interactions such as ligand field forces, will also cause splitting, but with the present means no greater resolution can be obtained.

We will now describe individual spectra and try to determine the energy levels of the constituting atoms. As it is felt that it is not possible with the present state of the theory to calculate levels with a precision better than 1 eV, the energies of the X-ray lines have been rounded off to an integer value. No attempt has been made to correct the spectra for instrumental distortion in order to obtain band widths.

A few data were taken from the literature; this regards some $K\beta'$ and $K\beta'''$ lines which we expect from the present theory to be extremely weak, furthermore data concerning oxygen spectra by Fischer[11], and K -absorption edge data.

4. RESULTS

(a) Calcium, electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$

The spectra of metallic calcium and calcium oxide were recorded (Fig. 1). We observe a marked shift only in $K\beta_5$. The binding energy ($B.E.$) of $1s$ electrons of Ca in CaO as determined by Hagström and Karlsson[4] is 4038 eV with respect to the Fermi level. The energy of O $K\alpha$ is 525 eV[11]. The energy of $K\beta_5$ is 4031 eV. Thus the oxygen $L_{II,III}$ level is situated at 7 eV, and the $B.E.$ of O in CaO is $525 + 7 = 532$ eV, which is in good agreement with the value 532 eV measured in MgO and Al_2O_3 [4, 5]. The residual charge on the oxygen ion is about equal for the three compounds (in electron units: -1.8 for MgO,

-1.6 for Al_2O_3 , -1.8 for CaO). The line $K\beta''$ at -15 eV with respect to $K\beta_5$, available in the literature[21], is explained by the $2s(O)-1s(Ca)$ transition; the L_1 level of oxygen then is situated at 22 eV; from electron spectroscopy this value is 23.7 eV[5]. The line $K\beta'$ is given in[21] at 4003 eV; the difference with the $K\beta_1$ energy, 10 eV, is used to promote an electron from the valence band at 5–7 eV to the conduction band, which then is centered at 4 eV above the Fermi level. This is in accordance with the position of the K absorption edge at 4041 eV in CaO[21]. The $K\beta'$ line is very weak, however, as we were not able to detect it. Two satellite peaks at 527 and 528 eV are visible in the oxygen spectrum as reported in[11]; these can be explained by the valence band transitions $3d(Ca)-1s(O)$ and $4s(Ca)-1s(O)$. The calcium oxide diagram is given in Fig. 6.

The calcium diagram is also given. The K absorption edge given in the literature, 4038 eV[21] is probably not quite correct, as this is the same value as the $B.E.$ of $1s$ electrons in CaO. On the basis of experimental evidence on the other metals the $B.E.$ in Ca is thought to be about 4036 eV. This is in accordance with findings by Finkelshtein and Nemnonov[22]. The levels of the Ca $1s$ and $3p$ electrons shift over the same amount when comparing CaO and Ca, which demonstrates the partly covalent character of the Ca–O bond, as a purely ionic bond would shift the K level more than the $M_{II,III}$ level.

(b) Titanium, electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$

The spectra of metallic titanium and titanium dioxide, rutile, were studied. The oxygen $K\alpha$ in TiO_2 is measured at 525 eV[11]. Assuming $B.E.$ $1s(O)$ to be 532 eV, the residual charge on the O ion being -1.5 electron units, we calculate $B.E.$ $1s(Ti)$ as $7 + 4962 = 4969$ eV. In titanium metal, $B.E.$ $1s$ is 4966 eV[6]. $K\beta''$ is due to the transition $2s(O)-1s(Ti)$; again, the oxygen L_1 level

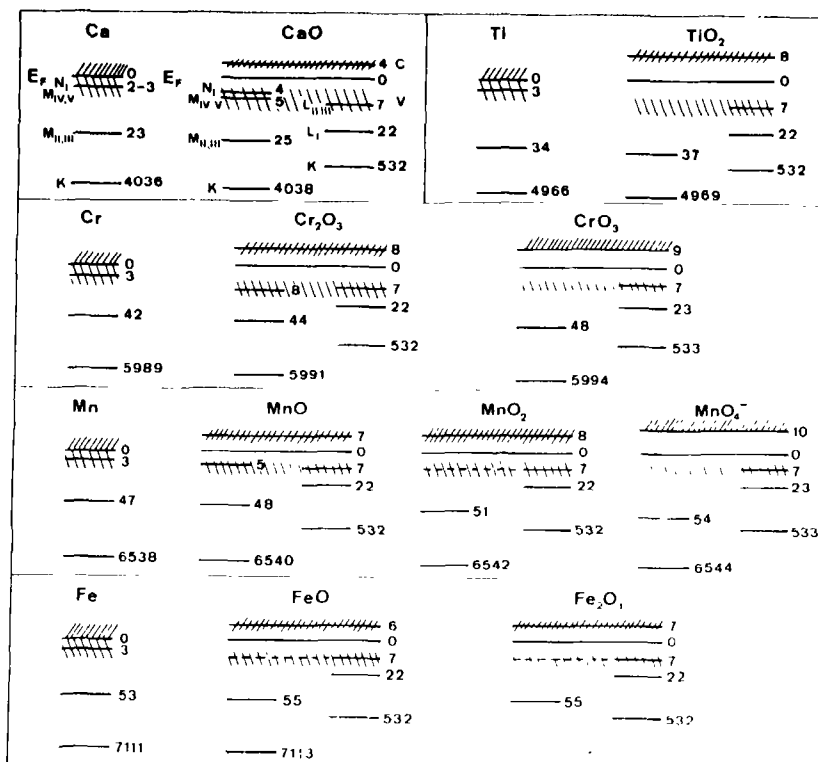


Fig. 6. Proposed energy levels in eV. For the sake of clarity, the notation in the diagrams, upper left corner of the 'the conduction'

is situated at 22 eV. According to theoretical computations by Ern and Switendick[2], in TiO there is a $2s(O)$ level at 22 eV from the Fermi level. In[21] is reported the line $K\beta'$ at 4916 eV; its difference with $K\beta$, 15 eV, is used to promote a valence electron at 7 eV to the conduction band at 8 eV, in satisfactory agreement with the value found for the K absorption edge: 4976 eV. As in CaO, the metal-oxygen bond is partly covalent, the $M_{II,III}$ level and the K level having both shifted about 3 eV, and the $M_{II,III}$ level even a trifle more than the K level. This in agreement with the well known fact[24] that titanium is more electronegative than calcium, and consequently forms a more covalent bond.

(III) oxide and chromium(III) oxide were also taken. The spectra of K_2CrO_4 and $K_2Cr_2O_7$ were also recorded, but proved to be identical to the spectrum of CrO_3 within the present experimental accuracy.

The oxygen $K\alpha$ in Cr_2O_3 is measured at 525 eV[11]; again assuming $B.E. 1s(O)$ to be 532 eV, the residual charge on the O ion being -1.6 electron units, we can plot the composite diagram for Cr_2O_3 . The K absorption edge is at 5999 eV, in good accordance with the scheme. In Cr_2O_3 , there are three unpaired $3d$ electrons; the transition prob-

ability to promote these electrons into the conduction band is greater than the transition probability for valence band $3d$ (metal) or $2p(O)$ electrons taking part in the chemical bond. Consequently we observe the $K\beta'$ line rather clearly in Cr_2O_3 , whilst it is extremely weak in CaO and TiO_2 . In CrO_3 on the other hand, all $3d$ electrons are shared, and $K\beta'$ again disappears. The oxygen spectrum in CrO_3 or K_2CrO_4 is not available, but there is the following indication in our own data that the oxygen levels will not be very different. The energy gap between $K\beta_5$ and $K\beta''$ is recognized as the energy gap of about 15 eV between the levels $L_{II,III}$ and L_I of oxygen; for Cr_2O_3 and CrO_3 it is 14 and 15.5 eV respectively, for MnO_2 and MnO_4^- 14 and 15 eV. Thus this gap is about 1 eV wider in CrO_3 and MnO_4^- . We may assume that the oxygen K and L_I levels shift over about 1 to 533 eV and 23 eV respectively, the residual charge on the oxygen being -1.1 electron unit. Thus the $L_{II,III}$ level will be at about 7 eV, in both CrO_3 and MnO_4^- . On this basis the composite diagram of CrO_3 is plotted. The K absorption edge is at 6004 eV [21] for K_2CrO_4 , the CrO_3 data not being found in the literature, thus the conduction band will have its edge at about 9–10 eV.

The energy level diagram of metallic chromium is plotted using the photo electron data of Nordberg *et al.* [6], *B.E.* $1s$ is 5989 eV.

The K level shifts 2 eV for Cr_2O_3 and 5 eV for CrO_3 ; the $L_{II,III}$ level shifts 2 eV for Cr_2O_3 and 6 eV for CrO_3 , indicating that the $Cr-O$ bond in Cr_2O_3 is partly covalent and in CrO_3 mainly covalent.

A very faint $K\beta'''$ line at 6000 eV is observed in Cr_2O_3 ; it is thought to be caused by an electron promoted to the conduction band falling back to the K level. As long as the selection rules holding for sublevels in the conduction band are obscure, this explanation is proposed. The $K\beta'''$ line is more prominent in ionic manganese and especially iron compounds.

(d) *Manganese, electron configuration* $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$

The materials examined were metallic manganese, green cubic manganese (II) oxide, manganese (IV) oxide or pyrolusite, potassium permanganate and lithium permanganate. The latter compound was used to study as carefully as possible the $K\beta_5$ part of the MnO_4^- spectrum, which is somewhat obscured by the first order potassium $K\alpha$ band. The $K\beta_1$ bands of lithium permanganate and potassium permanganate were identical.

The only oxygen $K\alpha$ energy available [11] is determined in MnO_2 : 525 eV. We may assume, by analogy with chromium, that the oxygen levels $L_{I,III}$ and K are situated at 7 and 532 eV respectively for MnO and MnO_2 and at 7 and 533 eV for MnO_4^- . Now we can plot the data in level diagrams. As regards the diagram for metallic manganese, *B.E.* $1s(Mn)$ was determined as 6539 eV by the photo electron method by Sokolowski [7]. The value 6538 eV fits better with our data, however, since this corresponds with K shifts of 2, 4 and 6 eV for Mn^{2+} , Mn^{4+} and Mn^{7+} respectively, whilst otherwise these shifts would amount to 1, 3 and 5 eV, which is less in accordance with the results on the other metals reported here. The *B.E.* determined from the K absorption edge is 6538 eV; possibly the material used in the photo electron data contained oxide.

The conduction bands in MnO and MnO_2 are centered at 7–8 eV; they must be rather wide since these compounds to some degree conduct electricity. This is in some agreement with the values found for the K absorption edges: 6543 and 6546 eV [21], although these data may not be too reliable. The absorption edge in $KMnO_4$ at 6554 eV indicates a large forbidden gap; no unoccupied $3d$ electrons can be promoted to the conduction band and $K\beta'$ does not appear.

The spectrum of MnO_4^- strikingly illustrates, that $K\beta_5$ is essentially due to an oxygen $L_{II,III} -$ manganese K transition, since the manganese $M_{IV,V}$ level would have shifted

at least 7–8 eV, the $M_{II,III}$ shifting 7 eV, and so would have caused a line with energy $6544 - (3 + 8) = 6533$ eV; instead we observe a line solely at 6538 eV. In the case of MnO and MnO_2 there are unoccupied 3d electrons, which could give a peak in the neighbourhood of $K\beta_5$. No splitting of peaks can with any certainty be observed, which, however, is also caused by the limited resolving power of the spectrograph. There could be an indication in the oxygen spectra. The oxygen $K\alpha$ band in MnO_2 is nearly symmetrical and thus the manganese $M_{IV,V}$ level will be situated at about 7 eV. This means a shift of 4 eV, which is quite reasonable, the $M_{II,III}$ level shifting also 4 eV. The MnO oxygen spectrum is not recorded; we would expect an extra peak, if any, at the high energy side.

(e) *Iron, electron configuration* $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$

The spectra of metallic iron, iron (II) oxide, iron (II,III) oxide or magnetite and α -iron (III) oxide or hematite were recorded. In order to obtain the $K\beta'$ position, the line profile of the $K\beta_1\beta'$ band was separated into its constituent parts by means of a standard $K\beta_1$ profile, for which was chosen the $K\beta'$ iron carbonyl $Fe(CO)_5$, a compound with a purely covalent bond. Metallic iron shows a broad band superimposed on the energy side of $K\beta_1$.

The oxygen spectra of Fe_3O_4 and Fe_2O_3 were recorded[11]; both show a peak at 525 eV. We assume *B.E.* oxygen 1s to be 532 eV, *B.E.* oxygen 2p 7 eV, and take *B.E.* 1s in metallic iron as 7111 eV from photoelectron data[25]. The energy level diagrams can now be constructed. The Fe_3O_4 diagram is not given in Fig. 5 as it is quite similar to the Fe_2O_3 diagram. The iron *K* level is seen to shift proportionally with the positive charge on the iron ion: 2 eV for FeO, 2.7 eV for Fe_3O_4 , 3 eV for Fe_2O_3 . The line $K\beta'$ is quite pronounced in all three oxides; most in Fe_2O_3 , least in FeO. Its intensity is highest when the 3d shell is half filled, i.e. when 5

electrons with parallel spins are present, as follows also from the manganese spectra, MnO having 5 3d electrons and MnO_2 3 3d electrons, and from cobalt and nickel oxide spectra. It stands to reason, that in this case an electron is most easily promoted to the conduction band, the energy for which is supplied by the $K\beta_1$ energy. The energy difference between $K\beta_1$ and $K\beta'$, in the compounds studied about 13–15 eV, should give rise to a peak in the absorption spectrum at the corresponding energy, i.e. at a wavelength of 800–900 Å. Unfortunately, practically no data are available in this region, so we have not been able to check this directly.

The $K\beta''$ lines are weak and only poorly resolved. The $K\beta'''$ lines can be clearly observed, especially in Fe_2O_3 ; its position at 7121 eV agrees well with the value calculated if we assume it to be a *K*-conduction band transition: $7114 + 7 = 7121$ eV. In FeO, $K\beta'''$ is so weak as to be nearly invisible; possibly the lifetime of an electron in the conduction band of semiconducting FeO is so long as to decrease the relative transition probability.

explained in the following way:
compounds with an accuracy of 1 eV.

(2) The metal *K* level changes to higher absolute values if the metal is brought into a higher oxidation state; for the oxides, this shift amounts to about 1 eV for each unit of formal positive charge. The charge in reality operative is less, covalent-ionic resonance redistributing the charge on the atom and its surroundings, but we can assume on the basis of the experiments that the resultant charge is in first approximation proportional to the formal charge for the same class of compounds (oxides).

(3) The M levels containing the valence electrons also shift but in a more complicated way, both charge and bond character exerting influence. The shift to higher absolute values is largest for covalent compounds.

(4) The oxygen levels are subject only to small variations. Due to cross-over transitions, rather complicated oxygen spectra can arise, however, as is demonstrated by Fischer [11], who recorded 28 oxygen K bands, but was unable to ascribe the difference in shape to any solid state properties. Only a carefully constructed composite diagram can explain or predict the oxygen spectrum.

(5) Since in the oxidic compounds the $K\beta_5$ line is essentially an oxygen $2p$ -metal $1s$ transition, its position is determined mainly by the metal K level, and consequently mainly by the valence of the metal ion. Hence we predict a linear dependence of the shift of the $K\beta_5$ maximum on the valence of the transition metal (the highest valences 6 and 7 excluded). For bi-, tri- and tetravalent titanium this was already found by Blokhin and Shuvaev [26], and for bi- and tri-valent iron by Kolobova, Nemnonov and Agapova [19].

(6) No such dependence can exist for the $K\beta_1$ line, resulting from a metal $3p$ -metal $1s$ transition; we can only expect a linear dependence, if the bond character and coordination remain approximately the same. While the $K\beta_1$ shifts are more complicated than the $K\beta_5$ shifts, the $K\beta_1$ intensity is much larger (40–100 times) than the $K\beta_5$ intensity; for the determination of valence and coordination both lines have their own merit.

Acknowledgements We are grateful to Professor Dr G. D. Rieck for his interest in the work and his remarks. One of us (H. M.) wishes to thank the Unilever Research Laboratory for a temporary assignment at the

Technical University in Eindhoven, where this research was carried out. Thanks are also due to Professor Rieck for his hospitality during this time.

REFERENCES

1. ERSHOV O. A. and LUKIRSKII A. P., *Fizika tverd. Tela* **8**, 2137 (1966).
2. IOMICHEV V. A., *Fizika tverd. Tela* **8**, 2892 (1966).
3. MENDEL H. and KOSTER A. S., *J. Phys. C*, in the press.
4. HAGSTRÖM S. and KARLSSON S. E., *Ark. Fys.* **26**, 451 (1964).
5. FAHMAN A., HAMRIN K., NORDBERG R., NORDLING C. and SIEGBAHN K., *Phys. Rev. Lett.* **14**, 127 (1965).
6. NORDBERG R., HAMRIN K., FAHMAN A., NORDLING C. and SIEGBAHN K., *Z. Phys.* **192**, 462 (1966).
7. SOKOŁOWSKI E., *Ark. Fys.* **15**, 1 (1958).
8. BEARDEN J. A., *Rev. mod. Phys.* **39**, 78 (1967).
9. SHUVAEV A. T. and CHECHIN G. M., *Izv. Akad. Nauk SSSR* **28**, 838 (1964).
10. BALLHAUSEN C. J., *Introduction to Ligand Field Theory*, McGraw-Hill, New York (1962).
11. FISCHER D. W., *J. chem. Phys.* **42**, 3814 (1965).
12. VAINSHTEIN É. F., BRII' M. N. and STARYI I. V., *Izv. Akad. Nauk SSSR* **20**, 784 (1956).
13. VAINSHTEIN É. F., OVRUTSKAYA R. M. and KOTIYAR B. I., *Fizika tverd. Tela* **7**, 2120 (1965).
14. BEST P. F., *J. chem. Phys.* **44**, 3248 (1966).
15. MENDEL H., *Proc. K. Ned. Akad. Wet.* **70**, 276 (1967).
16. MEN'SHIKOV A. Z. and NEMNONOV S. A., *Fiz. metall.* **14**, 187 (1962).
17. MEN'SHIKOV A. Z. and NEMNONOV S. A., *Fiz. metall.* **19**, 57 (1967).
18. BLOKHIN M. A., *Zh. éksp. teor. Fiz.* **9**, 1515 (1939).
19. KOLOBOVA K. M., NEMNONOV S. A. and AGAPOVA E. V., *Fizika tverd. Tela* **10**, 729 (1968).
20. MEN'SHIKOV A. Z., *Fiz. Metall.* **14**, 396 (1962).
21. LANDOLT-BÖRNSTEIN, *Zahlenwerte und Funktionen* Vol. 1, p. 4, Springer, Berlin (1955).
22. IINKELSHTEIN I. D. and NEMNONOV S. A., *Fiz. metall.* **22**, 843 (1966).
23. FRN V. and SWITENDICK A. C., *Phys. Rev.* **137**, 1927 (1965).
24. PAULING L., *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, New York (1948).
25. BEARDEN J. A. and BURR A. I., *Rev. mod. Phys.* **39**, 125 (1967).
26. BLOKHIN M. A. and SHUVAEV A. T., *Izv. Akad. Nauk SSSR* **26**, 429 (1962).

X-RAY $K\beta$ EMISSION SPECTRA AND ENERGY LEVELS OF COMPOUNDS OF 3D-TRANSITION METALS—II

NON-OXIDIC COMPOUNDS

A. S. KOSTER

Technical University, Eindhoven, The Netherlands

and

H. MENDEL

University of Ibadan, Nigeria

(Received 16 October 1969)

Abstract—The $K\beta$ emission spectra of various calcium, titanium, chromium, manganese and iron compounds were investigated by means of the fluorescent method. The origin of the lines found experimentally is discussed, their energies are given and used to construct composite energy diagrams. The dependence of the level positions on the chemical bond is shown, and an extrapolation is carried out to determine the charge on the metal ions in the pure metal.

1. INTRODUCTION

IN PART I of this study [1] the X-ray $K\beta$ spectra of calcium, titanium, chromium, manganese, iron and a number of the oxidic compounds of these elements were discussed. These spectra were obtained by the fluorescence method employing an apparatus commercially available. Composite energy level diagrams were derived using these measurements; they were put on an absolute scale by means of photoelectron data. In the diagrams, the shifts of the levels are closely connected to bond type and valence. In order to obtain further confirmation of the theory, expounded in part I, a number of non-oxidic compounds were examined, and the results of this investigation are given here. Special attention was given to compounds of rather extreme bond type, such as the carbonyl and cyanide complexes which contain covalent bonds, while fluorides are examples of essentially ionic substances.

2. EXPERIMENTAL

The samples used were either compounds commercially available or chemically anal-

ysed preparations of our own laboratory. Their purity was at least 96 per cent, except calcium carbide which was about 80 per cent.

The method of obtaining the spectra and the level positions was described in part

to $K\beta_1'$ the peaks to the low energy side of $K\beta_1$, and by $K\beta_1''$ the peak to the high energy side of $K\beta_1$.

The estimated error in $K\beta_1$ is 0.2 eV; in the other lines 0.4–0.6 eV. For ease of comparison the data for CaO , TiO_2 , Cr_2O_3 , MnO and Fe_2O_3 are included as they appear in [1].

3. RESULTS

(a) Calcium

The spectra of calcium fluoride and calcium carbide were recorded, in addition to the spectra of metallic calcium and calcium oxide

Table 1. Peak positions in eV and relative peak intensities

$I(K\beta''')$	$K\beta'''$	$K\beta$	$K\beta_1$	$K\beta''$	$K\beta_2$	$K\beta'$	$\frac{I(K\beta''')}{I(K\beta_1)}$	$\frac{I(K\beta_1)}{I(K\beta_2)}$	$\frac{I(K\beta')}{I(K\beta_1)}$
CaO		4031.5				4012.7			
CaF ₂		4030.4				4013.2			
CaC ₂		4032.5				4012.9			
TiO ₂		4961.8		4947.1		4931.6			
Na ₂ TiF ₆		4963.2	4957.8	4943.2		4931.8		0.20	
Cr ₂ O	6000.2	5983.8		5969.9		5946.9			0.50
CrF ₃	5997.8	5982.5				5947.5	0.09		0.15
K ₂ Cr(CN)		5984.8				5932.2	0.10		0.31
MnO		6533.2				6475.7			0.07
MnS		6533.9				6491.6			0.11
K ₂ MnF ₆	6548.8	6535.7				6475.6			0.06
K ₂ MnF ₆	6549.6	6536.5		6516.0		6475.2	0.14		0.13
K ₃ Mn(CN) ₆		6534.3		6516.9		6491.0	0.10		0.13
Fe ₂ O ₃	7120.6	7107.0		7093.1		7058.9			0.05
FeF ₃	7122.9	7108.2				7043.6	0.20		0.08
FeS		7107.0				7058.2	0.37		0.05
FeS ₂		7106.6				7057.6			0.14
K ₄ Fe(CN) ₆		7106.0				7056.8			0.08
K ₃ Fe(CN) ₆		7107.0				7057.2			
Fe(CO) ₅		7104.1				7044.3			0.025

which were already given in [1]. Shuvaev, Zyryanov and Gorskii have also investigated the fluorescent Ca spectra in CaO, CaF_2 and CaC_2 [2], and their experimental results on $K\beta_1$ are in agreement with ours. Their reported shifts of $K\beta_5$ differ from our observations, however. In order to draw the composite diagram for CaF_2 , it is necessary to know the binding energy (*B.E.*) of an electron in the compound. The energy of $F^- K\alpha$ has been measured by Fischer [3]: 677 eV, and *B.E.* of 1s electrons of fluorine in NaF is given by Hagström and Karlsson [4]: 685 eV. The residual charge of the fluoride ions in NaF and CaF_2 , calculated according to Pauling using electronegativities, is -0.97 and -0.95 electron units respectively, and thus the binding energies of F 1s electrons can be expected to be equal within the accuracy of 1 eV. The same argument was used to determine the composite diagram of MgF_2 in [5]. The levels K and $M_{II,III}$ for the F^- ion are placed at 685 and 8 eV respectively. The Ca-F bond being mainly ionic, the $K\beta_5$ line stems from a $2p(F)-1s(\text{Ca})$ transition, and thus the whole diagram can be constructed (Fig. 1). The K level of Ca is at 4038 eV, which is at about the same position as CaO. As a matter of fact, the residual charges on the Ca ion are almost equal ($+1.1$ electron units (e.u.) for CaO, $+1.90$ for CaF_2). The K level in both compounds being at almost the same position, the small shift of $K\beta_1$ reflects a small shift of the $M_{II,III}$ level, which in CaF_2 is slightly lower in absolute value than in CaO due to a less covalent bond. This is in agreement with the conclusions of our former paper [1].

There are two closely spaced high energy satellite lines in the fluorine spectrum of CaF_2 , which also can be found in other fluorides [3, 6, 7]. Their intensity seems to depend on the metal ion present; in the series $\text{LiF}-\text{NaF}-\text{KF}$ their intensity decreases. As long as the experimental evidence is scanty, nothing can be said about the origin

of these lines with certainty. They could be due to neutral atoms of fluorine as is suggested by O'Bryan and Skinner [6]. Their decreasing intensity in the series of the alkali fluorides, where the structure type remains the same (NaCl type), depicts the influence of the cation radius; the same effect can be observed in the series $\text{CaO}-\text{SrO}-\text{BaO}$ (NaCl type), where the same satellites seem to occur in the oxygen $K\alpha$ spectrum.

The position of $K\beta_1$ in CaC_2 is nearly the same as in CaO, as was noted by Shuvaev *et al.*; they could not explain this fact. Following the line of our previous arguments regarding the shift of the $K\beta_1$ emission line as depending upon bonding type (part I), we would expect the Ca ion to have a residual charge roughly equal to the charge in CaO. This can be understood by assuming the $\text{Ca}(4s)$ electron to have a large overlap with the lone electron in the $\text{C}(sp)$ hybrid giving an electron pair.

This is in accordance with the crystal structure, which is a distorted NaCl packing with a linear $\text{Ca}-\text{C}-\text{C}-\text{Ca}$ arrangement. The small positive charge on the

the carbon atoms have a small negative residual charge [5]. Taking *B.E.* 1s(C) in diamond as 283 eV, it follows that the *B.E.* 1s(C) of the acetylenic carbon atoms must be less than 283 eV. Assuming the *B.E.* 1s(Ca) in CaC_2 to be equal to the *B.E.* in the oxide, the upper level of the $K\beta_5$ emission line is $4038 - 4032 = 6$ eV. Thus the C $K\alpha$ line is expected to be less than $283.6 - 277$ eV. No C $K\alpha$ spectra in an acetylenic compound have been determined; other types of carbides [8] give a value of about 277 eV.

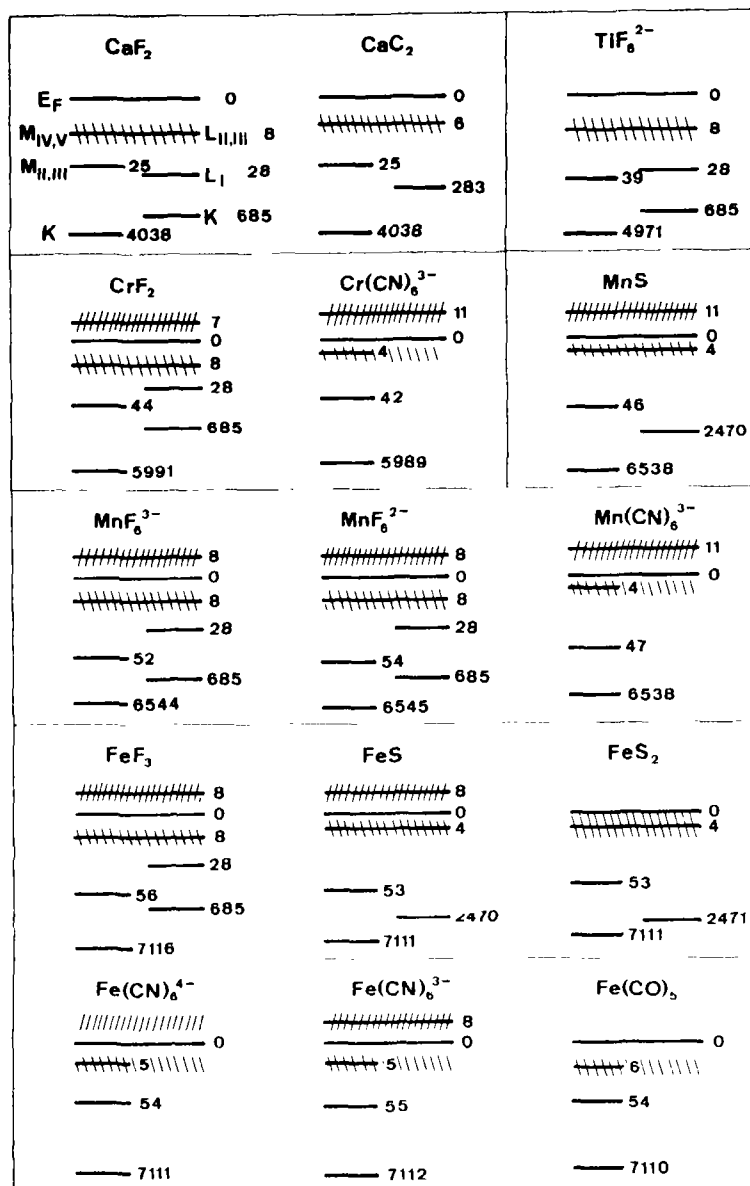


Fig. 1. Proposed energy levels in electron volt. For the sake of clarity, the notation of the diagrams is only indicated in the CaF_2 diagram. E_F is the Fermi level; the valence band and the conduction band are denoted by hatching.

(b) *Titanium*

The compounds Na_2TiF_6 and K_2TiF_6 were studied. These spectra are exactly the same, and thus purely represent the TiF_6^{2-} ion. The presence of fluoride ions gives rise

to the formation of $K\beta''$, which is a $2s(\text{F})-1s(\text{Ti})$ transition. The separation between $K\beta_5$ and $K\beta''$ is 20 eV, corresponding to the separation between the $L_{II,III}$ and L_I levels of the fluoride ion. The separation is the same in all fluorides, including MgF_2 which was investigated earlier[5].

Because of the strongly ionic character of the Ti-F bond, the residual charge on F being -0.9 e.u. we can place the fluoride K , L_I and $L_{II,III}$ levels at 685, 28 and 8 eV respectively, thereby defining the composite diagram of the TiF_6^{2-} ion. It follows that the titanium K level is at 4971 eV, which is 2 eV higher than the level at 4969 eV found in TiO_2 ; this is in agreement with the residual charge on the titanium ion (in TiO_2 : $+3.0$ e.u., in TiF_6^{2-} : $+3.5$ e.u.).

The band $K\beta_5$ can be separated into two components: the strongest, called $K\beta_5$, can be assumed to be connected to the $2p(\text{F})$ level, as 88 per cent of the $3d$ and $4s$ electrons are removed forming the Ti^{IV} ion; the other much smaller peak, called $K\beta_5'$, is thought to arise by the transition of the remaining 12 per cent of electrons mainly characterized by metal $3d$, $4s$ π functions. Thus there are two rather discrete levels in the valence band, separate about 5 eV. This splitting up of the band is hard to detect in the TiO_2 spectrum because $K\beta''$ interferes there, but seems indeed to be somewhat broader than in the fluoride. There are faint indications that $K\beta_5'$ also occurs in the chromium and manganese fluorides. In CaF_2 , however, there is no trace of it, although the resolving power of the apparatus would allow its observation; this is to be expected, no $3d$ electrons being present. In FeF_3 it can not be detected due to the limited resolution.

(c) Chromium

We investigated CrF_2 and $\text{K}_3\text{Cr}(\text{CN})_6$, both of which contain unpaired $3d$ electrons with parallel spins. In CrF_2 of mainly ionic type there are four of such electrons. The

complex ion $[\text{Cr}(\text{CN})_6]^{3-}$ is of covalent type, involving octahedral bond orbitals; two $3d$, one $4s$ and three $4p$ orbitals are available for use as bond orbitals, which leaves three unpaired electrons in the $3d$ orbital. According to the theory explained in our former paper[1], the energy of $K\beta_1$ is partly used to promote these unpaired electrons from the valence band into an excited state, which we can call the conduction band. The reduced $K\beta_1$ energy appears as a peak to the low energy side of $K\beta_1$, and the difference between $K\beta_1'$ and $K\beta_1$ is connected to the gap between valence band and conduction band. The line $K\beta'$ should show up in both compounds, as is indeed the case. The intensity of $K\beta'$ is found to be proportional to the number of unpaired $3d$ electrons, as is fully confirmed by the data given for Mn and Fe compounds. Unfortunately, however, the bands of $K\beta_1$ and $K\beta'$ overlap each other, which makes a reliable measurement difficult. As a 'standard profile' for Cr $K\beta_1$ we used the band of CrO_4 , which theoretically should not be contaminated with a $K\beta'$ band, and which,

Calculation

On the chromium ion being nearly equal in Cr_2O_4 and CrF_2 ($+2.2$ e.u. and $+1.8$ e.u. respectively), we can place the Cr K level at 5991 eV; this results in the following value of $K\beta_5$: $5991-8 = 5983$ eV (observed 5982.5 eV). As to $K\beta_1$, in CrF_2 the energy of the $L_{II,III}$ level decreases slightly as the Cr-F bond is less covalent, thus we expect a small shift to higher eV (observed shift is $+0.6$ eV).

Indicating the energy levels in mainly covalent compounds like the complex cyan-

ides is a more difficult task, because of a lack of carbon or nitrogen spectra and photoelectron data; furthermore the charge on the central metal ion is as yet only very imperfectly known. Pauling[9] assumes that in the cyano complexes the metal ion carries a slightly positive charge. Tentatively we would suggest to place the metal K levels of these covalent compounds approximately at the height of the metal K level of the metallic element, the atoms in the metal also carrying a small positive charge, as will be explained in a later section of this paper. Thus, the chromium levels K , $M_{II,III}$ and $M_{IV,V}$ in $K_3Cr(CN)_6$ are placed at 5989, 42 and 4 eV.

(d) Manganese

The spectra of MnS (synthesized from the elements), K_3MnF_6 , K_2MnF_6 and $K_3Mn(CN)_6$ were recorded.

The intensity of $K\beta'$ relative to the intensity of $K\beta_1$ is the same in MnO and MnS; both compounds contain 5 unpaired $3d$ electrons. The relative intensity of $K\beta'$ in K_3MnF_6 (4 $3d$ electrons), in K_2MnF_6 (3 $3d$ electrons) and in $K_3Mn(CN)_6$ (2 $3d$ electrons) decreases in this order, in accordance with the hypothesis. All these compounds have a large forbidden gap.

The fluoride (2s)-manganese (1s) transition, clearly visible as $K\beta''$ in the spectra of K_3MnF_6 and K_2MnF_6 , and the $K\beta_3$ fluoride (2p)-manganese (1s) transition enable us to construct the composite diagrams of these compounds. Again plotting fluoride

K , L_1 and $L_{II,III}$ at 685, 28 and 8 eV, we find for $B.E.$ $1s(Mn)$ in K_3MnF_6 6544 eV, in K_2MnF_6 6545 eV, which is in good agreement with the residual charges calculated for these compounds and the oxidic compounds: (Table 2).

The lines $K\beta'''$ can be seen clearly in the spectra of the complex fluorides, whilst they are invisible in the spectra of MnO and MnS. As was stated in part I[1], they are thought to be due to the transition of the electrons in the band of the excited states to the K level. These electrons were brought into this band by the absorption of X-ray quanta, for instance of $K\beta_1$ quanta, which gives rise to the formation of $K\beta'$. The salts of the complex fluorides being nearly perfect isolators, the lifetime of these promoted electrons is very short, and $K\beta'''$ shows up rather strongly. In compounds of higher conductivity, like MnO and MnS, this transition is less likely to occur.

In order to plot the composite diagram for MnS, we determined the position of the sulphur $K\beta$ maximum and found 2466 eV (elementary sulphur: 2464 eV). According to Nordling and Siegbahn[10], the change in $B.E.$ of sulphur $1s$ electrons is 4–5 eV per unit residual charge, and since the residual charge on the S ion is about -0.6 e.u., we may expect the S K level to have shifted from 2472 eV in elementary sulphur[4] to about 2470 eV in MnS. Thus the valence band containing the sulphur $3p$ electrons is at $2470-2466 = 4$ eV, and the manganese K level is calculated at $6534 + 4 = 6538$ eV,

Table 2

Compound	residual charge on Mn (e.u.)	position of K level (eV)	shift of K level with respect to the metal (eV)
MnO	+1.8	6540	2
MnO ₂	+2.4	6542	4
MnF ₆ ³⁻	+2.8	6544	6
MnO ₁	+3.0	6544	6
MnF ₆ ²⁻	+3.7	6545	7

which is in good correspondence with the residual charge on the Mn ion, +0.6 eV, as compared with oxides and fluorides.

The manganese levels in $K_3Mn(CN)_6$ are given with the same restrictions as the chromium levels in $K_3Cr(CN)_6$. Although MnS is also markedly covalent, the energy of $K\beta_1$ in $K_3Mn(CN)_6$ is 1 eV less than in MnS, which points to a much more covalent character of the former compound, the charges on the metal ions being about the same.

(e) Iron

We present results for FeF_3 and FeS as partly ionic compounds and for FeS_2 , $K_3Fe(CN)_6$, $K_4Fe(CN)_6$ and $Fe(CO)_5$ as mainly covalent compounds.

Again, the intensity of $K\beta'$ is seen to be connected with the number of unpaired 3d electrons; this band is present in FeF_3 (5 3d electrons), FeS (4 3d electrons) and $K_3Fe(CN)_6$ (1 3d electron), while it is absent in FeS_2 , $K_4Fe(CN)_6$ and $Fe(CO)_5$, where all electrons are engaged in *dsp* hybridisation. Careful comparison of the $K\beta_1\beta'$ profiles of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$, scaled upon each other, enable us to determine contribution of one 3d electron. The λ width of $Fe(CO)_5$ is of somewhat smaller width than those of FeS_2 and $K_4Fe(CN)_6$ indicating that in the latter substance a minor contribution of another bond is realized.

The construction of the composite diagrams of FeF_3 and FeS can be carried out as for the analogous manganese compounds. The fluoride being mainly ionic, the residual charge on F^- being -0.9 e.u., we take *B.E.* 1s (F) as 685 eV and *B.E.* 2p (F^-) as 8 eV, thus *B.E.* 1s (Fe) is $7108 + 8 = 7116$ eV. The energy gap between $K\beta_1$ and $K\beta'$ is 16 eV and this energy is used to promote the 3d electrons to the conduction band, centered at -8 eV. When these electrons fall back to the *K* level from this band (not necessarily from the centre of gravity of this

band), $K\beta'''$ is generated. In FeF_3 , this line is very pronounced.

We determined the energy of sulphur- $K\beta$ in FeS as 2466 eV. The residual charge on the S ion is about -0.5 e.u. and thus we may place the sulphur *K* level at 2470 eV. As in MnS, the valence band is at 4 eV, and thus the iron *K* level is found at $7107 + 4 = 7111$ eV, which is consistent with the other data on iron compounds.

In the mainly covalent compounds, the $K\beta_5$ band is sharper and the ratio $I(K\beta_5)/I(K\beta_1)$ is higher than for the ionic compounds. Obviously, due to covalent bonding more electrons of a sharper defined energy level are available than in the case of the ionic compounds where part of the electrons are removed to the anion sites, whence cross-over transitions are less likely to take place. Furthermore, occurrence of both one-atom transitions and cross-over transitions as in oxides blur out the sharpness of $K\beta_5$. In the order FeS_2 , $K_4Fe(CN)_6$, $Fe(CO)_5$, the energy of $K\beta_5$ is seen to decrease, pointing to an increasing degree of covalency.

Now experimental binding energies are available. For FeF_3 the *K* level is found to be 7111 eV, which is then $2471 - 2467 - 4$ eV, which is the iron *K* level at $7107 + 4 = 7111$ eV, in agreement with the idea that the metal *K* level in the covalent compounds is about equal or somewhat lower than the level in the pure metal. Tentatively we indicate the *B.E.*'s in the other iron compounds in Fig. 1. The decrease in $K\beta_5$ energy for the more covalent compounds is seen to be mainly caused by increase of the $M_{N,N}$ energy. The iron atom in $K_4Fe(CN)_6$ is seen to carry a somewhat higher charge than

in $K_1Fe(CN)_6$ because the separation between the K and $M_{II,III}$ level is larger.

4. DISCUSSION

(1) It has been shown by Nordling and Siegbahn[10], that the experimentally determined K shell binding energies when plotted against the residual charge on the atom fall approximately on a straight line. For sulphur, this line has been a slope of 4–5 eV per unit residual charge. From our paper on a number of oxides[5] it can be inferred, that the slope is about 3 eV/e.u. for oxygen. This correlation procedure can also be carried out for chromium, manganese and iron, where a sufficient number of substances has been investigated. These graphs are given in Fig. 2; indeed, straight lines can be drawn with a slope of about 3 eV/e.u., when the shift of the K level with respect to the pure metal is plotted against the residual charge in electron units. The lines do not pass through the origin, which means that the metal atom in the elementary state carries a small positive charge, between +0.8 and +1.0 e.u. This is in accordance with the notion that the metallic bond is described by an electron gas, moving between metal cations. From the graphs can be deduced the K shell binding energy of a free metal atom with zero charge; we find for Cr, 5987 eV; for Mn, 6536 eV; for Fe, 7109 eV.

(2) Generally, the ideas advanced in part I of this study are fully confirmed by the findings described in this part. Especially, the concept of the composite diagram enables us to explain facts at first sight contradictory, for instance, that $K\beta_5$ should shift to lower energy when comparing CaF_2 with CaO and to higher energy when comparing FeF_3 with Fe_2O_3 , or that $K\beta_1$ should shift to lower energy when comparing MnF_6^{2-} with MnO and to higher energy when comparing FeF_3 with Fe_2O_3 . The results of about thirty $K\beta$ spectra thus fit together in a consistent unity.

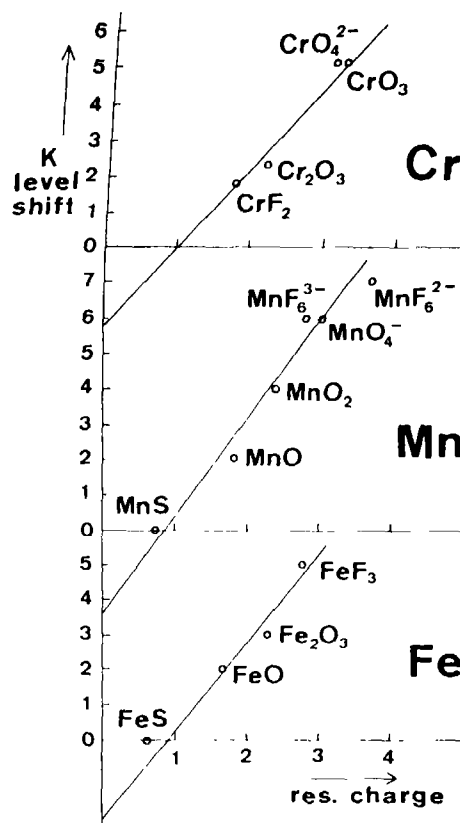


Fig. 2 Graph of the residual charge (in electron units) plotted against the shift of the K level (in eV) with respect to the metal.

REFERENCES

1. KOSTER A. S. and MENDEL H., *J. Phys. Chem. Solids* **31**, 2511 (1970).
2. SHUVAEV A. I., ZYRYANOV V. G. and GORSKII V. V., *Izv. Akad. Nauk SSSR* **28**, 731 (1964).
3. FISCHER D. W., *J. chem. Phys.* **42**, 3814 (1965).
4. HAGSTROM S. and KARLSSON S. E., *Ark. Fys.* **26**, 451 (1964).
5. MENDEL H. and KOSTER A. S., *J. Phys. C*, (In press).
6. O'BRYAN H. M. and SKINNER H. W. B., *Proc. R. Soc. Lond.* **A176**, 229 (1940).
7. MATISON R. A. and EHLEERT R. C., *Adv. X-ray Anal.* **9**, 471.
8. FISCHER D. W. and BAUN W. L., *Adv. X-ray Anal.* **9**, 329.
9. PAULING L., *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, New York (1948).
10. NORDLING C. and SIEGBAHN K., *Rev. Roum. Phys.* **11**, 797 (1966).

TIME LAGS IN THE BREAKDOWN OF NaCl AT HIGH TEMPERATURES

D. B. WATSON

Robert Gordon's Institute of Technology, School of Electrical Engineering, Schoolhill, Aberdeen, Scotland

and

W. HEYES

Electrical Engineering Department, University of Salford, England

(Received 29 September 1969, in revised form 20 February 1970)

Abstract—The relationship between time lag and applied field was investigated at high temperatures for NaCl crystals by applying a single 1.8000 μ sec impulse to each crystal, of sufficient magnitude to cause breakdown. The observed time lag cannot be satisfactorily explained in terms of joule heating alone and an ionic space charge mechanism is proposed.

1. INTRODUCTION

THE RELATIONSHIP between temperature and the electric strength of alkali halide crystals consists of two regions. At low temperatures breakdown is considered to be electronic in nature and the electric strength increases slowly as the temperature is raised, in qualitative agreement with the theories of Fröhlich [1] and of von Hippel [2], while at high temperatures the electric strength decreases comparatively quickly. The transition temperature between these two regions is sharply defined; it is influenced by the form of the applied voltage and may be completely suppressed over the temperature range investigated by using steeply rising impulse voltages, in which case the electric strength continues to rise [3–5]. Also, for a given voltage wave-form the transition temperature varies widely with the type and degree of impurity content of the dielectric. Cooper, Higgin and Smith [6] found that when 0.022 per cent of lead, a divalent impurity, was added to KCl the critical temperature was depressed from about 110°C to –120°C. Monovalent impurity, however, had little effect. In view of these effects it is not surprising that complete agreement between the results of different studies is difficult to obtain.

The existence of a high temperature region, where the electric strength of alkali halides decreases with rise in temperature, is predicted by Fröhlich's high temperature theory of electronic breakdown [7]. It can also be explained both in terms of impulse thermal breakdown due to the increase in ionic conductivity at high temperatures, or as a consequence of ionic space charge which en-

the measured time lags were of the order of a few microseconds, indicating that at least up to 220°C impulse thermal breakdown does not take place. The effect of divalent impurities on the transition temperature, however, showed the important role of ionic conductivity, and breakdown above the critical temperature was concluded to be conditioned by the onset of ionic space charge. At higher temperatures Heyes and Watson [8] discovered time lags of the order of milliseconds in the impulse breakdown of NaCl. The

variation of time lags with applied field was similar to that of impulse thermal breakdown, although at the higher fields the time lags were too short to be directly explicable in terms of energy input alone. Thus the high temperature region has not yet been satisfactorily explained. The purpose of the present investigation was the determination of the relationship between time lag and applied field in the high temperature breakdown region of NaCl in order to throw further light on the mechanisms leading to breakdown.

2. EXPERIMENTAL METHOD

The specimens were cleaved cubes of NaCl about 2 cm side, drilled from two opposite faces with a twist drill leaving a gap between the two in-line recesses. A spherical end to each recess was made by hand with a dentist's round burr of 0.64 mm dia. This operation was carried out under a microscope which enabled the gap between the recesses to be reduced to 0.07 mm to an accuracy of ± 0.005 mm. To form silver electrodes in intimate contact with the crystal a colloidal silver preparation was painted onto the surface of each recess, and this was allowed to dry at

room temperature before the specimens were placed in the furnace.

The specimens were allowed to stand in the furnace at the operating temperature for 18 hr before application of the test voltage, when the temperature of each specimen was within 3°C of the required value.

A single stage impulse generator was used, giving a 1:8000 μsec voltage wave-form. The relationship between charging voltage and output voltage was determined by means of sphere gaps.

3. EXPERIMENTAL RESULTS

The multiple impulse breakdown field was determined by applying a series of 1:8000 μsec voltage impulses, starting at about 50 per cent of the expected breakdown voltage and increasing in increments of 0.5 kV. The mean value for about 6 specimens at each temperature is shown in Fig. 1 which also shows the minimum impulse thermal breakdown field calculated from equation (3). Above 270°C the agreement between the experimental and calculated breakdown field is quite good.

The time lag to breakdown, from the crest of the impulse wave to the collapse of voltage,

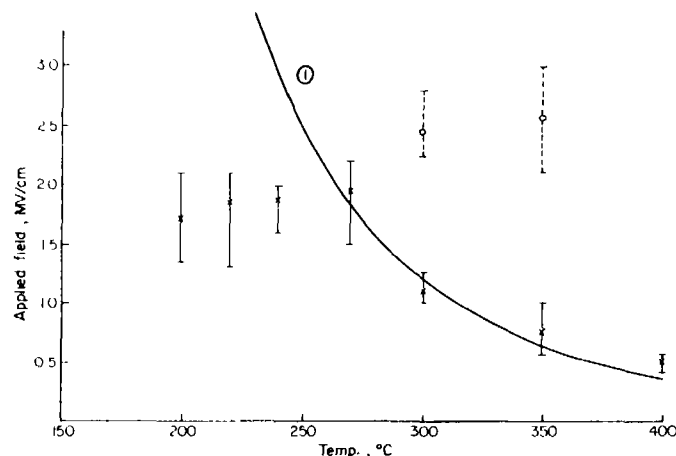


Fig. 1. Electric strength of NaCl as a function of temperature. The vertical lines indicate the range of measured values X Multiple impulse breakdown O Single impulse, breakdown near crest of wave. (1) Calculated impulse thermal breakdown field.

was measured to an accuracy of $0.1 \mu\text{sec}$ on a 10 MHz counter-timer, and its value was checked against an oscillogram of the impulse voltage wave-form at breakdown. Below 240°C only time lags of a few microseconds were measured, indicating that breakdown had occurred near the crest of the voltage wave. At 240°C some specimens registered time lags as long as $3000 \mu\text{sec}$, and at higher temperatures almost all the time lags were of this order. These long time lags, together with the rapid fall in electric strength, could be considered indicative of impulse thermal breakdown.

The relationship between time lag and applied field was investigated at 300 and 350°C by applying to each specimen a single $1:8000 \mu\text{sec}$ impulse voltage large enough to cause breakdown. Most specimens broke down on the wave tail and the time lags for these are plotted against the peak value of the applied field in Fig. 2. The calculated time lag for impulse thermal breakdown is also shown for the purpose of comparison. It can be seen that as the field was increased the experimental time lags decreased far more rapidly than the calculated values.

At higher fields specimens broke down on the crest of the impulse wave, and breakdown for these was considered to be electronic in nature since time lags of a few microseconds are too short for thermal breakdown.

The average values of electric strength for such specimens, included in Fig. 1 at 300 and 350°C , indicate that the electric strength of NaCl continues to rise with increasing temperature when the processes leading to long time lags are inhibited.

4. DISCUSSION

The impulse thermal breakdown strength can be estimated assuming that heat loss by thermal conduction is negligible. The rate of rise of temperature is then

$$\frac{d\theta}{dt} = \frac{E^2}{s} \exp\left(-\frac{2t}{T}\right) \sigma_0 \exp\left(-\frac{b}{\theta}\right) \quad (1)$$

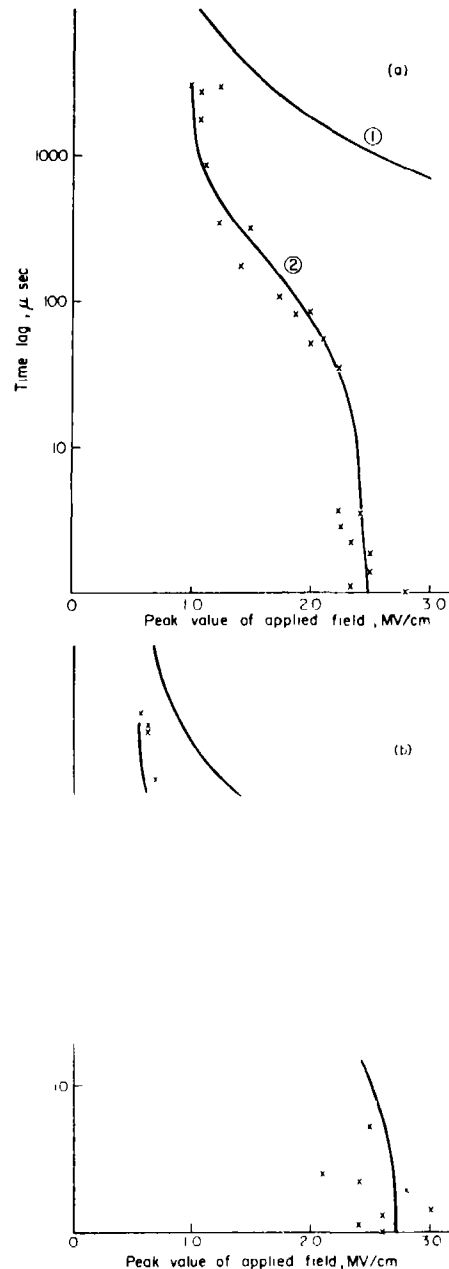


Fig. 2. Time lags for single impulse breakdown of NaCl at temperatures (a) 300°C , (b) 350°C . (1) Calculated for impulse thermal breakdown, (2) Calculated for space charge controlled breakdown mechanism, x Experimental values.

where

$$E \exp\left(-\frac{t}{T}\right)$$

is the exponentially decaying applied field, s is the specific heat per unit volume and $\sigma_0 \exp(-b/\theta)$ is the law relating electrical conductivity to the absolute temperature θ . If $b \gg \theta$ equation (1) can be integrated to give approximately

$$\frac{\theta_1^2}{b} \exp\left(\frac{b}{\theta_1}\right) = \frac{E^2 \sigma_0 T}{2s} \left[1 - \exp\left(-\frac{2t_m}{T}\right) \right]. \quad (2)$$

Here t_m is the time required for the temperature to reach θ_m , the value at breakdown, and θ_1 is the ambient temperature. Since heat losses have been neglected, the lowest value of E at which the temperature rises to θ_m is found by putting $t_m \rightarrow \infty$ in equation (2). The lowest impulse thermal breakdown field is then

$$E_{\min} = \left(\frac{2s}{\sigma_0 T b} \right)^{1/2} \theta_1 \exp\left(\frac{b}{2\theta_1}\right). \quad (3)$$

For NaCl $\sigma_0 = 0.5 \Omega^{-1} \text{cm}^{-1}$ and $b = 10,000$ [9][10]; $s = 2 \text{ W cm}^{-1}$; and putting $T = 8,000 \mu\text{sec}$ the following values of $E_{\min}$ are obtained:

Temperature (°C)	200	225	250	275	300	325	350	375	400
$E_{\min}$ (MV/cm)	6.1	3.8	2.5	1.7	1.2	0.85	0.64	0.46	0.37

This characteristic is shown in Fig. 1.

In view of the high fields required for impulse thermal breakdown at low temperatures it is most likely that below about 270°C the electric strength of NaCl when determined by applying a series of 1:8000 μsec voltage impulses of slowly increasing magnitude will be electronic in nature. Above 270°C the experimental values agree quite well with those predicted by equation (3). This agreement must, however, be viewed with caution. The impulse thermal condition only requires that the temperature is raised sufficiently to produce an order of magnitude increase in the electrical conductivity and about 90 per cent of the pulse time is taken in achieving this. The further rapid rise in temperature

occurs in a relatively short time[11]. It may well be that final breakdown takes place before the melting temperature is attained either due to a fall in the electronic strength at high temperatures or to the enhancement of the field by ionic space charge due to the sudden increase in ionic conductivity. Thermal run-away may not be responsible for initiating final disruption of the dielectric, although breakdown must be associated with a significant rise in lattice temperature because of the long time lag involved. At fields higher than $E_{\min}$ the impulse thermal time lag is given by

$$t_m = \frac{-T}{2} \log_e \left[1 - \left(\frac{E_{\min}}{E} \right)^2 \right]. \quad (4)$$

The impulse thermal time lag plotted against the peak value of applied field, in Fig. 2, was calculated using values of $E_{\min}$ obtained from equation (3). At 2 MV/cm the calculated time lag is of the order of hundreds of micro-seconds. Such a high field should, however, give rise to electronic breakdown with time lags far too short for thermal breakdown. In fact, in the high temperature region, if break-

down at low fields is due to thermal instability, the relation between time lag and applied field should be described by equation (4) until the field is high enough to cause electronic breakdown when a sharp discontinuity would result as the time lags drop to a few micro-seconds. In contrast, the experimental time lags fell continuously as the field was increased, from a few thousand microseconds at $E_{\min}$ to less than one microsecond at fields high enough to cause wave-crest breakdown. Unless the electrical conductivity is strongly dependent on field strength it is difficult to see how the impulse thermal breakdown theory could explain the measured time lags.

It is possible that the field within the speci-

men is distorted by the formation of an ionic space charge if the rate at which ions are transported to the electrodes exceeds their rate of discharge. A positive space charge may thus accumulate close to the cathode because of the greatly increased mobility of positive ions at the temperatures of this investigation. The space charge therefore enhances the field in the cathode region causing electronic breakdown when the cathode field reaches some critical value.

A possible type of relationship between time lag and applied field, associated with such a breakdown mechanism, may be determined by assuming that the space charge is uniformly distributed within a layer of thickness x adjacent to the cathode.

If at any instant the average field throughout the specimen is E_{av} , the field at the cathode is E_1 , and the field in the neutral body of the specimen is E_2 , then

$$E_{av}d = E_2d + (E_1 - E_2) \frac{x}{2}$$

where d is the distance between the anode and the cathode. When the total charge cumulated in the layer of thickness x adjacent to the cathode is q , then,

$$E_1 - E_2 = \frac{q}{\epsilon_0 \epsilon_r}$$

hence

$$E_1 = E_{av} + \frac{q}{\epsilon_0 \epsilon_r} \left(1 + \frac{x}{2d}\right) \quad (5)$$

and

$$E_2 = E_{av} - \frac{q}{\epsilon_0 \epsilon_r} \left(\frac{x}{2d}\right). \quad (6)$$

The rate at which charge accumulates at the cathode may be assumed to be:-

$$\frac{dq}{dt} = \eta \sigma E_2$$

where σ is the electrical conductivity and η

is the fraction of the total charge transported to the cathode which is not immediately discharged. Thus

$$\frac{dq}{dt} = \eta \sigma \left(E_{av} - \frac{qx}{\epsilon_0 \epsilon_r 2d} \right).$$

The fields E_1 and E_2 , however, vary with time due to both the build up of space charge and the exponential decay of the applied field, which has the form

$$E_{av} = E \exp\left(\frac{-t}{T}\right)$$

where E is the peak value of the applied field. Therefore

$$\frac{dq}{dt} + \frac{\eta \sigma q x}{\epsilon_0 \epsilon_r 2d} = \eta \sigma E \exp\left(\frac{-t}{T}\right)$$

thus

$$q = \frac{\eta \sigma E \left[\exp\left(-\frac{\eta \sigma x t}{\epsilon_0 \epsilon_r 2d}\right) - \exp\left(\frac{-t}{T}\right) \right]}{\left[\frac{1}{T} - \frac{\eta \sigma x}{\epsilon_0 \epsilon_r 2d} \right]} \quad (7)$$

$$\frac{1}{\epsilon_0 \epsilon_r} \left[\frac{1}{T} - \frac{\eta \sigma x}{\epsilon_0 \epsilon_r 2d} \right] \quad (8)$$

These expressions show that the charge and the cathode field rise to maximum values thereafter falling as the specimen discharges.

It is now assumed that breakdown is initiated when the cathode field reaches some value E_b . Two extreme cases are considered, the first being that the peak value of applied field is almost as great as E_b , and the cathode

field rises to the breakdown value in a very short time. The equation relating short time lags with applied field is then obtained by using the first two terms of the Taylor series for the exponentials in equation (8), and

$$E_B = E \left[1 - \frac{t}{T} + \frac{\eta \sigma t}{\epsilon_0 \epsilon_r} \left(1 - \frac{x}{2d} \right) \right].$$

The linear relationship of Fig. 3 between the reciprocal of applied field and the experimental time lag up to about 150 μsec has, therefore, the gradient

$$m = \frac{E_B}{\frac{\eta \sigma}{\epsilon_0 \epsilon_r} \left(1 - \frac{x}{2d} \right) - \frac{1}{T}}.$$

The values of m are 720 and 370 $\mu\text{sec MV cm}^{-1}$ at 300 and 350°C respectively, and the corresponding values of E_B , at zero time lag are 2.5 MV/cm and 2.7 MV/cm. Since $T \approx 8000 \mu\text{sec}$ the term $1/T$ is negligible. Thus

$$\frac{\eta \sigma}{\epsilon_0 \epsilon_r} \left(1 - \frac{x}{2d} \right) = \frac{E_B}{m} \quad (9) \quad \text{where}$$

where E_B and m are experimentally derived quantities.

In the second case an order of magnitude estimate of the unknown ratio $x/2d$ is obtained by considering the lowest applied field

$$E_{av} = E_0 \exp \left(-\frac{t}{T} \right)$$

that will cause breakdown. The total charge is at its maximum $q_{\max}$ at some time t' where, by equating to zero the time derivative of equation (7),

$$q_{\max} = \epsilon_0 \epsilon_r \frac{2d}{x} E_0 \exp \left(-\frac{t'}{T} \right).$$

If it is assumed that E_1 reaches its maximum value E_B at the same time then, using equation (5),

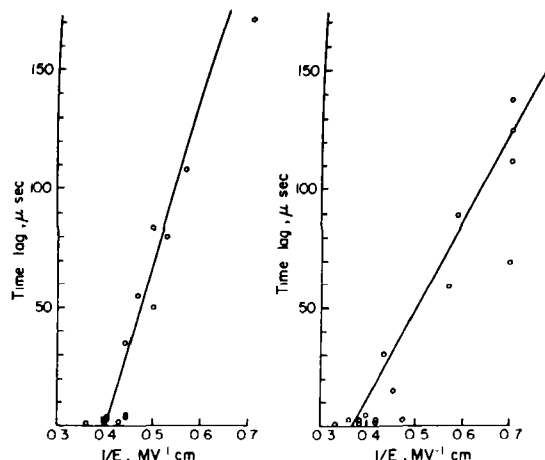


Fig. 3 Relationship between single impulse time lags and reciprocal of applied field at temperatures, (a) 300°C, (b) 350°C

$$E_B = \frac{2d}{x} E_0 \exp \left(-\frac{t'}{T} \right).$$

Hence

$$\frac{x}{2d} = \frac{E'_0}{E_B} \quad (10)$$

$$E'_0 = E_0 \exp \left(-\frac{t'}{T} \right).$$

Using equations (9) and (10) the general relationship of equation (8) between time lag t and applied field $E \exp(-t/T)$ can now be written

$$E_B = E \left\{ \exp \left(-\frac{t}{T} \right) + \frac{\frac{E_B}{m} \left[\exp \left(\frac{-t}{T} \right) - \exp \left(-\frac{t}{m \left(\frac{1}{E'_0} - \frac{1}{E_B} \right)} \right) \right]}{\frac{1}{m \left(\frac{1}{E'_0} - \frac{1}{E_B} \right)} - \frac{1}{T}} \right\}. \quad (11)$$

The longest time lags t' are about 3000 μsec and the values of E_0 are 1.0 MV/cm and 0.55 MV/cm at 300 and 350°C respectively. Substitution of the experimental values of m , E'_0 , E_μ and T in equation (11) gives the relationship between time lag and applied field shown in Fig. 2, which compares favourably with the experimental time lag distribution.

5. CONCLUSION

The time lags are not satisfactorily explained in terms of joule heating alone and the proposed ionic space charge mechanism gives results in reasonable agreement with the experimental values. It is concluded that the formation of an ionic space charge leads to breakdown in a time too short to allow the relatively large temperature rise required for impulse thermal breakdown. At the highest breakdown fields very little joule heating takes place, but at the lowest breakdown

fields the time lags are sufficiently long to allow appreciable heating before the space charge enhanced field reaches the critical value, and the distinction between this space charge mechanism and impulse thermal breakdown becomes less marked.

REFERENCES

1. FROHLICH H. *Proc. R. Soc. A* **160**, 230 (1937)
2. VON HIPPEL A. *Ergebn. exakt. Naturw.* **14**, 79 (1935)
3. VON HIPPEL A. and ALGER R. S. *Phys. Rev.* **76**, 127 (1949)
4. KONOROVA F. A. and SOROKINA I. A. *Soviet Phys. solid St.* **7**, 1186 (1965)
5. KUCHIN V. D. *Rep. Akad. Sci. USSR* **114**, 301 (1957)
6. COOPER R., HIGGIN R. M. and SMITH W. A. *Proc. phys. Soc.* **B76**, 817 (1960)
7. FROHLICH H. *Proc. R. Soc.* **188**, 493 (1947)
8. HEYES W. and WATSON D. B. *Nature, Lond.* **220**, 572 (1968)
9. SMEKAL A. *Handb. Phys.* **24**, 881 (1933)
10. HANSCOMB J. R., KAO K. C., CAIDFRWOOD J. H., O'DWYER J. J. and FMTAGE P. R. *Proc. phys. Soc.* **88**, 425 (1966)
11. O'DWYER J. J. *The Theory of Dielectric Breakdown of Solids*. Oxford Universities Press, Oxford (1964)

FERROMAGNETIC AND SPIN WAVE RESONANCE AT HIGH PRESSURE*

T. A. UHRIG†

Case Western Reserve University, Cleveland, Ohio 44106, U.S.A.

(Received 19 December 1969; in revised form 19 February 1970)

Abstract—The pressure dependence of the magnetization (+0.105%/kbar), g value (+0.094%/kbar), and exchange stiffness D (+0.054%/kbar) have been measured by ferromagnetic and spin wave resonance from one bar to five kilobars at room temperature in 80–20 permalloy. Since the film is evaporated on a sapphire substrate, the film is not deformed hydrostatically but is strained +0.0293%/kbar in thickness and –0.0106%/kbar in the transverse directions. When the pressure dependence of the magnetization is compared to hydrostatic determinations, the magnetization is found to be an anisotropic function of strain. Using the general Heisenberg model, the hydrostatic strain dependence of D (+0.067%/kbar) is derived from the experimental results. For the nearest neighbor Heisenberg model, the atomic distance dependence of the interatomic exchange $\{d(\ln J)/d(\ln a) \approx -5.2\}$ is calculated from the results and compared to the pressure dependence of the Curie temperature, and the magnetic Grüneisen factor. The spin wave resonance results are also analyzed using the short range, single band itinerant electron model to determine the strain dependence of the band splitting parameter Δ (+0.048%/kbar).

1. INTRODUCTION

THE MAGNETIC properties of the ferromagnetic transition metals as a function of atomic spacing is of theoretical and experimental interest. Recent theoretical papers include band structure calculations for copper as a function of lattice spacing[1] and the itinerant electron theory of the pressure dependence of the Curie temperature[2]. Experimental studies over a broad range of ferromagnetic effects have been measured as a function of pressure: Curie temperature[3–5], spontaneous magnetization[4–7], anisotropy constants[7,8], coercive field[8], and domain structure[8]. Magnetic resonance studies vs. pressure have included nuclear magnetic resonance[9], parallel ferromagnetic resonance[10], and just recently spin wave resonance[11].

In this paper we present the results and analysis of pressure dependent ferromagnetic

and spin wave resonance for the magnetization, g -value, and exchange stiffness of permalloy at room temperature. {The sample subjected to pressure is a permalloy film

and the theoretical Herring–Kittel equation[12].

$$H_n = \frac{\omega}{\gamma} + 4\pi M - \frac{D}{\gamma h} k_n^2, \quad (1)$$

where

H_n = resonant magnetic field of n th mode

ω = microwave frequency in rads./sec.

γ = magnetomechanical ratio

$4\pi M$ = saturation magnetization

D = exchange stiffness

* This research was supported in part by the Air Force Office of Scientific Research under grant AF-AFOSR-68-1484.

† Present address: Bell Telephone Laboratories, Columbus, Ohio 43213, U.S.A.

$k_n = n\pi/l =$ wave vector of n th SWR
 $l =$ thickness of film.

The experimentally measured quantity is the pressure derivative of each resonance.

$$\frac{dH_n}{dP} = -\frac{\omega}{\gamma} \frac{d(\ln \gamma)}{dP} + 4\pi M \frac{d(\ln 4\pi M)}{dP} - \frac{D}{\gamma \hbar} k_n^2 \left[\frac{d(\ln D)}{dP} - \frac{d(\ln \gamma)}{dP} + 2 \frac{d(\ln k_n)}{dP} \right], \quad (2)$$

where

$$\frac{d(\ln k_n)}{dP} = \frac{d(\ln n)}{dP} - \frac{d(\ln l)}{dP}.$$

In performing the differentiation between equations (1) and (2), it is assumed that the frequency ω is independent of pressure. During the experiment, the frequency changed slightly ($\Delta\omega/2\pi \approx 30$ MHz out of $\omega/2\pi = 8.730$ GHz). Thus the experimental resonant fields are corrected to a common frequency of 8.730 GHz. The pressure dependence of n is assumed to be zero (which follows if the magnetization remains strongly pinned at the surface).

The first two terms in equation (2) are simply the pressure dependence of the so-called uniform (or $k=0$) perpendicular resonance and involve the pressure dependences of $4\pi M$ and γ . A second relationship can be obtained between these parameters from the pressure dependence of the parallel resonance field H_p as given by Kittel's equation (13),

$$\frac{\omega}{\gamma} = \sqrt{H_p(H_p + 4\pi M)},$$

$$-\frac{\omega}{\gamma} \frac{d(\ln \gamma)}{dP} = \frac{1}{2} \sqrt{H_p(H_p + 4\pi M)} \left[\frac{d(\ln H_p)}{dP} + \frac{1}{H_p + 4\pi M} \left(\frac{dH_p}{dP} + \frac{d4\pi M}{dP} \right) \right], \quad (4)$$

Thus the pressure dependence of γ [or $g = 2\gamma/\gamma(g=2)$] and $4\pi M$ are determined from the parallel and perpendicular uniform resonances versus pressure.

The last terms in equations (1) and (2) describe the separation of the spin wave spectrum from uniform resonance. Its pressure dependence (equation (2)) involves the pressure dependence of D , γ , and l . Thus to isolate $d(\ln D)/dP$, one must obtain $d(\ln \gamma)/dP$ (from uniform parallel and perpendicular resonance) and $d(\ln l)/dP$ (from a mechanical analysis of the film thickness as done in the next section, or ideally from direct measurement during the experiment). In the previous study of SWR vs. pressure by Gustafson and Phillips [11], the pressure dependence of γ was ignored, and the quoted results lumped the pressure dependence of D and l together as $d\{\ln(D/l^2)\}/dP$. We have taken all these effects into account and obtained $d(\ln D)/dP$.

Our result is correlated with the results of other pressure experiments (in particular the Curie Temperature T_c) using the Heisenberg and itinerant electron models. The use of the Heisenberg model for a metal is of course suspect, but it gives a straight forward method of comparing results using one parameter (the exchange energy J for a nearest neighbor model). Thus the Heisenberg model is useful for comparing $d(\ln D)/dP$ measured by SWR and $d(\ln T_c)/dP$, and gives an order of magnitude agreement.

The itinerant electron model is much more reasonable for the metallic ferromagnet, but at the expense of increased complexity and results that depend on several parameters except in special limits. The results are analyzed to give the pressure dependence of the band splitting Δ using a single parabolic energy band whose effective mass tensor varies with applied strain. This result is consistent with the theoretical range predicted using Kanamori's low density limit for U_{eff} [14] (see Section 2). It is currently difficult to extract any further information (such as the ratio of the intra-atomic exchange to band-

width) from the SWR pressure results because sufficiently realistic theories are not available.

Before giving a more detailed discussion of the experiment, results, and analysis in Sections 3-5 respectively; the Heisenberg and itinerant electron theories of D for the experimental nonhydrostatic conditions will be developed in the next section.

2. THEORY

Mechanically the film strains are determined by the film being thin compared to the substrate, and by the surface dimensions of the film being completely determined by the substrate as if the substrate was unconstrained under the hydrostatic pressure. Assuming that the film and substrate both obey a linear isotropic stress-strain relation, the film strains can be derived [15] as

$$\begin{aligned}\delta_t &= -\frac{1}{3}\beta_{\text{sub}}P, \\ \delta_z &= \frac{1}{1-\sigma_{\text{film}}^2} \left[\frac{1}{E_{\text{film}}} (1-3\sigma_{\text{film}}^2-2\sigma_{\text{film}}^3) \right. \\ &\quad \left. - \frac{2}{3}(\sigma_{\text{film}} + \sigma_{\text{film}}^2)\beta_{\text{sub}} \right] P, \quad (5)\end{aligned}$$

where

- δ_t = transverse strain
- δ_z = thickness film strain
- P = pressure
- β_{sub} = volume compressibility of substrate
- E_{film} = Young's modulus of film
- σ_{film} = Poisson's ratio of film.

Using the bulk elastic constants for an 80-20 permalloy film [16] and a sapphire substrate [17] (as used in this experiment), the strains are

$$\begin{aligned}\delta_t &= -1.06 \times 10^{-4} \text{ kbar}^{-1} P \\ \delta_z &= -2.93 \times 10^{-4} \text{ kbar}^{-1} P, \quad (6)\end{aligned}$$

while the hydrostatic film strain would be

$$\delta_h = -2.08 \times 10^{-4} \text{ kbar}^{-1} P, \quad (7)$$

Heisenberg model

For the Heisenberg model, the strain dependence of D is found by starting with the general Hamiltonian, expressing the magnon energy for small q in terms of the strain tensor, and performing a polycrystalline average to obtain $D(\delta)$ for a polycrystalline film.

Assuming only translational invariance from site to site, the general Heisenberg Hamiltonian $\mathcal{H}$ in the presence of a magnetic field H in the z direction is [18]

$$\mathcal{H} = -\sum_{j\alpha} J_{\alpha} S_j \cdot S_{j+\alpha} - 2\mu H \sum_j S_{jz}, \quad (8)$$

where

- J_{α} = interatomic exchange between spins separated by the vector α
- S_j = the spin on the j th site measured in units of $\hbar$
- $\mu = (g/2)\mu_B$ = the magnetic moment per unit $\hbar$ of spin
- μ_B = the Bohr magneton ($eh/2mc$)
- H = internal magnetic field in z direction
- S_{jz} = the z component of the spin on the

If the ferromagnet is strained uniformly with no shear, the position vectors α between sites are

$$\alpha = (\vec{1} + \vec{\delta})\alpha_0 \quad (10)$$

where

$$\vec{\delta} = \text{the strain tensor} = \begin{bmatrix} \delta_t & 0 & 0 \\ 0 & \delta_t & 0 \\ 0 & 0 & \delta_z \end{bmatrix}$$

α_0 = the position vectors between the unstrained sites.

The magnon energy for this strained magnetic crystal is found by expanding the magnon energy to first order in small strains,

$$\hbar\omega_q = S \sum_{\alpha_0} [J_{\alpha_0}(\mathbf{q}, \alpha_0)^2 + 2J_{\alpha_0}(\mathbf{q}, \alpha_0)(\mathbf{q} \cdot \hat{\delta} \cdot \alpha_0) + \nabla_{\alpha} J_{\alpha_0} \cdot \hat{\delta} \cdot \alpha_0 (\mathbf{q} \cdot \alpha_0)^2] + 2\mu H, \quad (11)$$

This gives the magnon energy for a strained single crystal Heisenberg ferromagnet. But the experiment is performed on a polycrystalline sample. Thus it is necessary to average the magnon energy over all the random grain orientations. For propagation in the z direction (observed in SWR) and for the interatomic exchange J_{α} varying as the magnitude of α or

$$\nabla_{\alpha} J_{\alpha_0} = \left(\frac{dJ_{\alpha}}{d\alpha} \right)_{\alpha_0} \alpha_0, \quad (12)$$

the polycrystalline magnon energy is

$$\hbar\omega_q = 2\mu H + D_0(1 + 2\delta_z + (\frac{1}{2}\delta_z + \frac{1}{2}\delta_r)A)q^2, \quad (13)$$

where

$$D_0 = S \sum_{\alpha_0} \frac{1}{3} J_{\alpha_0}^2 \alpha_0^2$$

$$A = \frac{1}{D_0} S \sum_{\alpha_0} \frac{1}{3} \left(\frac{dJ_{\alpha}}{d\alpha} \right) \alpha_0^3.$$

The preceding discussion is for a general non-nearest neighbor Heisenberg ferromagnet of arbitrary crystal symmetry. For a simple cubic, face centered cubic, or body centered cubic solid with nearest neighbor exchange, the parameters D_0 and A are evaluated as

$$D_0 = 2SJ a^2, \quad (14)$$

$$A = d(\ln J)/d(\ln a),$$

where a is the lattice constant and J is the nearest neighbor exchange.

Itinerant electron model

This discussion of the itinerant electron

(*IE*) model will be restricted to the short range, strong correlation, one band model with no interatomic exchange. The Hamiltonian [19] for this *IE* model is

$$\mathcal{H} = \sum_{k,\sigma} \epsilon_k n_{k\sigma} + U \sum_R n_{R\uparrow} n_{R\downarrow}, \quad (15)$$

where

- k = momentum or wavevector of electron
- ϵ_k = band energy of the electrons
- $n_{k\sigma}$ = number operator for electrons of momentum k and spin σ
- $n_{R\sigma}$ = number operator for electrons on the Wannier site R with spin σ
- U = effective intra-atomic exchange.

In the random phase approximation, the *IE* model gives the integral equation for the magnon energy [20]

$$1 = \frac{\Delta}{N_s} \sum_k \frac{n_{k\uparrow} + n_{k\downarrow}}{\epsilon_k + \Delta - \hbar\omega_q}, \quad (16)$$

where

- N_n = number of atoms
- N_{σ} = number of electrons of spin σ
- $N = N_{\uparrow} + N_{\downarrow}$ = total number of electrons
- $N_s = N_{\uparrow} - N_{\downarrow}$ = number of excess up spin electrons
- $n_{k\sigma}$ = number of electrons of momentum k and spin σ
- $\Delta = U(N_s/N_n)$ = the band splitting.

As the ferromagnet is strained, the energy bands are deformed. Heine [21] has theoretically determined that the widths of energy bands should vary as a^{-5} , where a is the lattice constant. Recent energy band calculations for copper as a function of lattice spacing by Davis, Faulkner and Joy [1] verify that the energy differences do vary linearly with lattice spacing and the variation is a^{-5} .

This discussion is restricted to a ferromagnet with a completely aligned ground state and a single energy band which is spherical for

zero strain. As the ferromagnet is strained, the energy band is assumed to become elliptical while remaining undistorted in the k plane perpendicular to the strain. Thus the energy band is given by

$$\epsilon_k = \frac{\hbar^2}{2} \mathbf{k} \cdot \bar{\xi} \cdot \mathbf{k}, \quad (17)$$

where $\bar{\xi}$ is the strain dependent reciprocal mass tensor. Since $k_{\max}$ (the momentum at the zone boundary) varies as a^{-1} and the band width (the energy difference between $k=0$ and $k_{\max}$) varies as a^{-5} , the reciprocal mass tensor is assumed to be

$$\xi = \frac{1}{m_0^*} (1 - 3\delta), \quad (18)$$

where m_0^* is the unstrained effective mass.

For this band structure, the strain dependent Fermi energy ϵ_f is

$$\epsilon_f = \epsilon_{f_0} (1 - \frac{10}{3}\delta_1 - \frac{1}{3}\delta_2), \quad (19)$$

where

$$\epsilon_{f_0} = \frac{\hbar^2}{2m_0^*} (6\pi^2 n)^{2/3}$$

n = electronic density.

The integral equation for the magnon energy is solved for small q giving

$$\hbar\omega_q = \frac{\hbar^2}{2m_0^*} \left[1 - \frac{4\epsilon_f}{5\Delta} \right] (1 - 3\delta_2) q^2, \quad (20)$$

where the strain dependence of ϵ_f is given above and the strain dependence of Δ will be determined experimentally.

To obtain an idea of the expected pressure dependence of Δ , let us consider a low electronic density and use Kanamori's approximation for the effective exchange U [14],

$$U = \frac{U_0}{1 + U_0 t} \quad (21)$$

where

U_0 = intra-atomic exchange

$$t = \frac{1}{2} \int_{\epsilon_f}^W \frac{\rho(\epsilon)}{N_a \epsilon} d\epsilon$$

$\rho(\epsilon)$ = electronic density of states for a single spin

W = band width.

Taking the density of states of the parabolic band as $\propto \epsilon^{1/2}$ for ϵ less than W and zero for ϵ greater than W , the band splitting is

$$\Delta = \frac{N_s}{N_a} \frac{U_0}{1 + \frac{3}{2} \left[1 - \left(\frac{\epsilon_f}{W} \right)^{1/2} \right] \frac{U_0}{W}}. \quad (22)$$

The intra-atomic exchange U_0 is practically independent of strain since it is the overlap of wavefunctions localized on the same site, and N_s/N_a is constant for our single strong ferromagnetic band. In addition the strain dependence of W and ϵ_f should be equal since the average strain dependence of W over all states is required. Thus the only remaining (or non-cancelling) strain dependence is in the $1/W$ factor in the denominator. Depending on the

strain dependence of U_0 (as it does using Kanamori's approximation), the pressure dependence of Δ (and thus Δ) is bounded by the pressure dependence of U_0 ($\propto 0$) and the pressure dependence of W .

3. DESCRIPTION OF EXPERIMENT

The heart of this experiment is a beryllium copper pressure vessel containing a sapphire microwave cavity (Fig. 1). The idea of using a conical sapphire microwave cavity to seal one end of a pressure vessel and to admit micro-

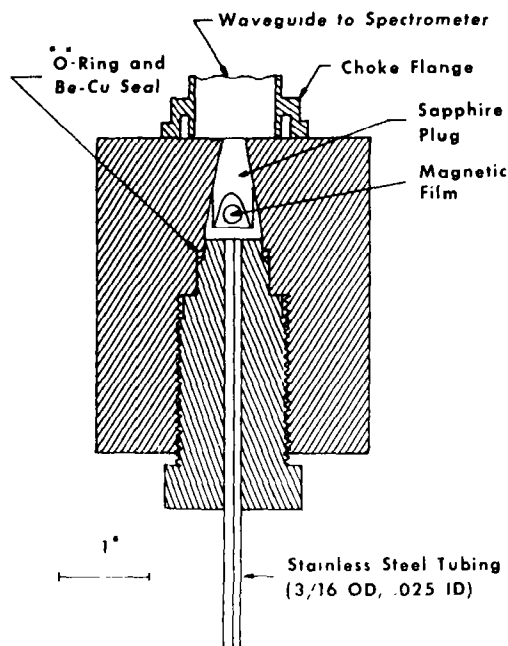


Fig. 1. Spin wave resonance pressure vessel.

wave radiation to a pressurized sample was originated by Goodrich, Everett and Lawson [22]. But for spin wave resonance, the conical sapphire design is changed so that the sample can be oriented perpendicular to the magnetic field. This is done by increasing the sapphire size and placing four polished flats parallel to its axis. The permalloy film is evaporated on one of these faces which allows the magnetic field to be oriented either perpendicular or parallel to the film. To maintain a high Q and to confine the microwave fields to the sapphire, the entire sapphire (except for the circular driven end) is coated with a layer of copper.

The microwave spectrometer is a standard reflected power X -band spectrometer which is set up for 'derivative traces' using field modulation (30 G peak to peak at 24 Hz) and lockin detection. The klystron frequency is stabilized to the sapphire cavity's resonant frequency and the actual frequency is monitored by a micrometer driven wavemeter.

The permalloy film (80% Ni-20% Fe, 3500

Å thick) is vacuum evaporated onto the heated sapphire (250°C) through a 5-mm dia. contact mask from an aluminum oxide coated tungsten wire basket (to avoid alloying). The film is annealed at 250°C for 2½ hr under vacuum to remove stresses and other imperfections. Finally the copper coating is added by evaporating a thin layer of copper and electroplating the remainder.

4. EXPERIMENTAL RESULTS

The experimental data is analyzed as outlined in the introduction and the results are presented in Table 1. The pressure dependence of D is found to be best determined by fitting the pressure dependence of each resonance to equation (2) (the pressure derivative of the SWR equation), rather than computing D for each pressure and then determining the pressure dependence. Using this method, the pressure dependences of modes 1-4 deviate from n^2 while only modes below 3 deviate appreciably from the quadratic dependence of their resonant fields H_n at any particular pressure.

During the experiment, the measured pressure dependences were not entirely repeatable. They decrease with pressure cycling and for each cycle are greater for increasing pressure than decreasing pressure. These effects are believed to be due to various mechanical relaxation processes and work hardening associated with the nonhydrostatic film strain.

Table 1. Experimental results for the strain conditions $\delta_r = -2.93 P \times 10^{-4} \text{ kbar}^{-1}$ and $\delta_t = -1.06 P \times 10^{-4} \text{ kbar}^{-1}$

X	$X(P=0) (10^{-4} \text{ kbar}^{-1})$	$\frac{d(\ln X)}{dP}$	$\frac{d(\ln X)}{d(\ln V)}$
$H(\text{parallel})$	0.79 kOe	-25	+5.0
$H(\text{perpendicular})$	13.19 kOe	+6.0	-1.19
$4\pi M$	10.23 kOe	+10.5	-2.02
σ_m	—	+5.5	-1.08
g	2.11	+9.4	-1.86
D	$41.5 \times 10^{-10} \text{ erg-cm}^2$	+5.4	-1.07

5. DISCUSSION

The zero pressure values of $4\pi M$ and g agree with the bulk values of Borzorth[23] and Kittel[24], and the zero pressure exchange stiffness D compares favorably with other spin wave resonance determinations [25-27].

While there is no data to compare with the pressure dependence of g , the experimental nonhydrostatic pressure dependence of the magnetization can be compared to the hydrostatic pressure dependence of the magnetic moment per atom (or per gram) σ_m . For 80-20 permalloy, Ebert and Kussman found $d(\ln \sigma_m)/d(\ln V) = +0.7$. The present experimental value is -1.08 . This difference is due to the fact that the magnetization is not just a function of volume, but is an anisotropic function of strain. {A much greater difference (as would be expected) has been observed by squeezing a pure nickel disk directly by piston action, which gave $d(\ln \sigma_m)/dP = +360 \times 10^{-4}$ kbar⁻¹ [28] compared to -2.8×10^{-4} kbar⁻¹ for nickel under hydrostatic pressure[6].}

Heisenberg discussion of D

The general Heisenberg theory of Section 2 (equation (13)) is used to compute the hydrostatic pressure dependence of D (see Table 2).

Table 2. Results using the Heisenberg M (starred data for the nearest neighbor approximation)

Hydrostatic $\frac{d(\ln D)}{dP}$	6.7×10^{-4} kbar ⁻¹
$\frac{d(\ln J)}{d(\ln a)}$	-5.2^*
γ_m	1.7^*

Our value for the hydrostatic pressure dependence of the exchange stiffness D is in agreement with the values found by Gustafson and Phillips [11] for the nickel iron alloys.

For the nearest neighbor Heisenberg model with cubic symmetry, $d(\ln J)/d(\ln a)$ is com-

puted from the experimental results and also from the pressure dependence of the Curie temperature. Since the Curie temperature T_c is proportional to J [24],

$$T_c = \frac{2}{3k} S(S+1)JN_n, \quad (23)$$

where

k = Boltzmann constant

N_n = number of nearest neighbors,

the fractional change of T_c and J with pressure are equal provided S is constant. Using the interpolated Curie temperature results of Patrick [3] for 80-20 permalloy, $d(\ln J)/d(\ln a)$ is -1.6 while this experiment gives -5.2 . This poor agreement is attributed to neglecting long range exchange effects in the nearest neighbor approximation.

The nearest neighbor Heisenberg model also gives a relationship between the pressure dependence of J and the 'magnetic Grüneisen factor' γ_m as given by White [29],

$$\gamma_m = \beta_m v K / C_m$$

$$C_m = \text{magnetic specific heat}$$

This experiment gives $\gamma_m = 1.7$ which is in good agreement with the total Grüneisen factor for permalloy between $\frac{1}{2}$ and 2 (from a crude interpolation of White's [29] values of $+2.0$ for permalloy, -11 for 40Ni60Fe and -20 for 35Ni65Fe).

Itinerant electron discussion of D

It is very difficult to obtain reasonable and consistent estimates of the parameters in the

IE model developed in Section 2 because of the simplified single parabolic band model. Thus the experimental results are analyzed using the magnon energy equation of Thompson and Myers for nickel [30]. Assuming the same pressure dependences as calculated in the simple theory, the Thompson-Myers equation for D is

$$D = \frac{\hbar^2}{2m_0^*} \left[1 - 0.706 \frac{\epsilon_f(\delta)}{\Delta(\delta)} \right] (1 - 3\delta_z), \quad (25)$$

where

$$\begin{aligned} m_0^*/m &= 5.71 \\ \epsilon_f(\delta) &= \epsilon_{f0}(1 - \frac{10}{3}\delta_t - \frac{5}{3}\delta_z) \\ \epsilon_{f0} &= 0.540 \text{ eV} \\ \Delta(0) &= 0.783 \text{ eV} \\ \frac{\epsilon_{f0}}{\Delta(0)} &= 0.69. \end{aligned}$$

It is noted that the $\frac{1}{3}$'s numerical factor in equation (20) has been replaced by 0.706 in Thompson-Myers equation (25) because of the nonparabolic nature of the actual bands.

Using the calculated strains (equation (6)), the pressure dependence of the Fermi energy is $8.4 \times 10^{-4} \text{ kbar}^{-1}$, and the experimental results give the effective mass and pressure dependence of the band splitting tabulated in Table 3. The measured pressure dependence of Δ ($4.7 \times 10^{-4} \text{ kbar}^{-1}$) lies within the predicted range (Section 2) between zero and the pressure dependence of ϵ_f ($8.4 \times 10^{-4} \text{ kbar}^{-1}$).

To conclude the discussion of D , one might ask what contribution the volume dependence of D has on the temperature dependence of D through the thermal expansion coefficient

$$\frac{1}{D} \frac{\partial D}{\partial T} \bigg|_P = \frac{1}{D} \frac{\partial D}{\partial T} \bigg|_V + 3 \frac{\partial(\ln D)}{\partial(\ln V)} \bigg|_P \frac{1}{V} \frac{\partial V}{\partial T} \bigg|_P. \quad (26)$$

Using Fannenwald and Weber's $(1/D)(\partial D/\partial T)|_P = 5 \times 10^{-4} / ^\circ\text{C}$ for 81-19 permalloy at room temperature [25] and the thermal expansion coefficient of 80-20 permalloy ($12.3 \times 10^{-6} / ^\circ\text{C}$) [16], the constant volume $(1/D)(\partial D/\partial T)$ value is $-4.6 \times 10^{-4} / ^\circ\text{C}$. Thus

Table 3. Results using the itinerant electron model with $4\epsilon_f/5\Delta = 0.487$ at zero pressure

m_0^*/m_e	14.7
$\frac{d(\ln \epsilon_f/\Delta)}{dP}$	$3.6 \times 10^{-4} \text{ kbar}^{-1}$
$\frac{d(\ln \epsilon_f)}{dP}$	$8.4 \times 10^{-4} \text{ kbar}^{-1}$
$\frac{d(\ln \Delta)}{dP}$	$4.8 \times 10^{-4} \text{ kbar}^{-1}$

the volume dependence has only an 8 per cent contribution to the temperature dependence of D at constant pressure and room temperature in permalloy.

6. CONCLUSIONS

The pressure dependences of the magnetization $4\pi M$, g value, and exchange stiffness D have been measured from 1 atm to 5 kbar at room temperature in 80-20 permalloy (see Table 1). The film was not deformed hydrostatically due to its constraint to the substrate, but was strained $-2.93 \times 10^{-4} \text{ kbar}^{-1}$ in thickness and $-1.06 \times 10^{-4} \text{ kbar}^{-1}$ in the transverse direction. This is in contrast to the isotropic strain of a hydrostatically deformed film of $2.08 \times 10^{-4} \text{ kbar}^{-1}$.

The results displayed a hysteresis with pressure and a decreasing pressure dependence from run to run. These are attributed to the effects of long time constant mechanical relaxation processes in the film possibly due to the nonhydrostatic applied strain. Possible solutions to these problems are to float the film or to evaporate the film on a low shear strength substrate so the film is subjected to hydrostatic conditions.

The experimental pressure dependences of the magnetization and exchange stiffness are compared with other pressure results and theoretical models. When the magnetization results are compared with the hydrostatic measurements of $d(\ln \sigma_m)/d(\ln V)$, it is observed that the magnetization is a highly anisotropic function of strain (i.e. the mag-

netization is not a function of volume only). Similarly it would not be unexpected if g were also an anisotropic function of strain, but there is no data available for comparison.

For the multi-neighbor Heisenberg model, a general relationship is derived between the isotropic and anisotropic strain dependence of D (Section 2). Using the nearest neighbor model, $d(\ln J)/d(\ln a)$ is calculated from the experimental results (-5.2). This is used to calculate the magnetic Grüneisen factor (1.7) which compares favorably with White's [29] value between $\frac{1}{2}$ and 2. But the nearest neighbor Heisenberg model gives poor agreement between our result and the pressure dependence of the Curie Temperature (which gives $d(\ln J)/d(\ln a) = -1.6$) [3].

The itinerant electron analysis using a single parabolic band is based upon the energy bandwidths varying as a^{-5} as predicted by Heine [21] and verified for copper energy bands by Davis, Falkner, and Joy [1]. Using estimates of the Fermi energy and band splitting at 1 atm, the pressure dependence of the band splitting is calculated from the experimental results ($4.8 \times 10^{-4} \text{ kbar}^{-1}$), and compares favorably with the expected theoretical range.

Acknowledgement—The author wishes to thank L. D. Thompson for his guidance and assistance during the course of this research.

REFERENCES

1. DAVIS H. I., FALKNER J. S. and JOY H. W., *Phys. Rev.*, **167**, 601 (1968).
2. LANG N. D. and EHRENREICH H., *Phys. Rev.*, **168**, 605 (1968).
3. PATRICK I., *Phys. Rev.*, **93**, 384 (1954).
4. BLOCH D. and PAUTHENIER R., *J. appl. Phys.*, **36**, 1229 (1965).
5. FUJIWARA H., OKAMOTO I. and IATSU-MOTO F., In *Physics of Solids at High Pressures* (Edited by C. I. Tomizuka and R. M. Emrick), pp. 261–271. Academic Press, New York (1965).
6. EBERL H. and KUSSMAN A., *Z. Phys.*, **38**, 437 (1937).
7. KAWAI N. and SAWAOKO A., *Rev. scient. Instrum.*, **38**, 1770 (1967).
8. IFSNIK A. G. and SANDLER M., *Phys. Status Solidi*, **17**, 753 (1966).
9. BENFEDER G. B., *Magnetic Resonance at High Pressures*, p. 19. Interscience, New York (1963).
10. EVLERT G. F. and LAWSON A. W., In *Physics of Solids at High Pressures* (Edited by C. I. Tomizuka and R. M. Emrick), pp. 252–260. Academic Press, New York (1965).
11. GUSTAFSON J. C. and PHILLIPS I. G., *Phys. Lett.*, **29A**, 273 (1969).
12. HERRING C. and KITTTEL C., *Phys. Rev.*, **81**, 869 (1951).
13. KITTTEL C., *Phys. Rev.*, **73**, 155 (1948).
14. KANAMORI, *Prog. theor. Phys., Kyoto*, **30**, 275 (1963).
15. UHRIG T. A., *Solid State Group Tech. Rep. No. 69-3*, Case Western Reserve University (1969).
16. MARSH J. S., *The Alloys of Iron and Nickel*, Vol. 1, pp. 111, 161, McGraw-Hill, New York (1938).
17. HART H. V. and DRICKAMER H. G., *J. chem. Phys.*, **43**, 2265 (1965).
18. KITTTEL C., *Quantum Theory of Solids*, pp. 49–74. Wiley, New York (1963).
19. HERRING C., In *Magnetism: Exchange Interactions among Itinerant Electrons* (Edited by G. T. Rado and H. Suhl), Academic Press, New York (1966).
20. IZUYAMA T., KIM D. I. and KUBOR T., *J. phys. Chem.*, **70**, 1225 (1966).
21. HEINE, *Phys. Rev.*, **163**, 876 (1967).
22. WEBER R. and LANSING W., *J. Phys. Chem.*, **140**, A498 (1965).
23. STACEY E. D., *Can. J. Phys.*, **34**, 304 (1956).
24. WHITE G. K., In *Physics of Solids at High Pressures* (Edited by C. I. Tomizuka and R. M. Emrick), pp. 222–224. Academic Press, New York (1965).
25. THOMPSON E. D. and MYERS J. J., *Phys. Rev.*, **153**, 574 (1967).

THE BOLTZMANN EQUATION FOR (111) VALLEYS IN GERMANIUM†

S. CHOU

Division of Engineering and Applied Physics, Harvard University, Cambridge, Mass 02138, U.S.A

(Received 23 July 1969; in revised form 29 January 1970)

Abstract—A numerical solution is presented for the usual model of electron transport in (111) valleys in *n*-Ge, with electric fields in the (100) direction. Calculations are for 77°K, with optical and acoustic deformation potential intravalley scattering considered. The effects of acoustic energy loss are quantitatively examined.

1. INTRODUCTION

THE 'USUAL MODEL' of electron transport in the (111) valleys in *n*-Ge has been described in the review book of Conwell[1]. The Boltzmann equation may be reduced to a set of coupled differential equations (equations (5.5.3) and (5.5.4) of Ref. [1]). These equations have in the past been given only approximate treatments for the case of high fields. In particular, the work of Reik and Risken[2] is based on certain assumptions regarding the form of the distribution functions, from which current saturation is predicted at high fields. In this paper a more rigorous solution is given to the same equations.

2. THE BOLTZMANN EQUATION

In this section the notation used is summarized. The assumptions involved in the formulas are discussed in Ref. [1], and will be repeated here.

Four (111) parabolic minima with $m_l = 1.64 m_0$ and $m_t = 0.082 m_0$ are assumed. Letting the zero of energy be the bottom of the (111) valleys, and defining

$$\Delta \mathbf{k} = \mathbf{k} - \frac{\pi}{a} (111), \quad (1)$$

the energy-wavevector relationship is given by

$$\epsilon = \frac{\hbar^2}{2} \left\{ \frac{(\Delta k)_x^2}{m_l} + \frac{(\Delta k)_y^2}{m_t} + \frac{(\Delta k)_z^2}{m_l} \right\} \quad (2)$$

where $\hat{z}$ is taken in the (111) direction.

We consider the case of electric field in the (100) direction, so that in a coordinate system defined by $\hat{x}, \hat{y}$ and $\hat{z}, \hat{z}$

$$\mathbf{E} = \langle -\sqrt{\frac{2}{3}}, 0, \sqrt{\frac{1}{3}} \rangle E \quad (\text{where } E = |\mathbf{E}|)$$

$$\Delta \mathbf{k} = \langle \Delta k_x, \Delta k_y, \Delta k_z \rangle. \quad (3)$$

Transforming to a momentum space such that constant energy ellipsoids become spheres, as was done by Reik and Risken[2], we can introduce an 'effective field' and an 'effective wave-

expanded in Legendre polynomials $P_l(\cos \angle(\Delta \mathbf{k}, \mathbf{E}))$:

$$f(\Delta \mathbf{k}^+) = f_0(\epsilon) + g(\epsilon) P_1(\cos \angle \Delta \mathbf{k}^+, \mathbf{E}^+) + \text{terms not considered.} \quad (6)$$

The formal Boltzmann equation is

$$-\frac{e}{\hbar} \mathbf{E} \cdot \nabla_{\mathbf{k}} f(\mathbf{k}) + \left[\frac{\partial f}{\partial t} \right]_{ac} + \left[\frac{\partial f}{\partial t} \right]_{mp} = 0 \quad (7)$$

†Research supported in part by Joint Services Contract 920-7309-2.

‡We choose $\hat{x} = 1/\sqrt{6}(\hat{z}11)$, $\hat{y} = 1/\sqrt{2}(011)$, $\hat{z} = 1/\sqrt{3}(111)$

where ϵ is negative. In the square brackets are represented collision terms due to acoustic and optical deformation potential scattering. Equivalent intervalley scattering need not be considered when each of the (111) valleys is equivalent with respect to the electric field, since it is weak. We need only solve for the distribution functions and drift velocities for one of the valleys.

Each collision term may be written

$$\left[\frac{\partial f}{\partial t} \right] = \left[\frac{\partial f_0}{\partial t} \right] + P_1 (\cos \angle \Delta \mathbf{k}^*, \mathbf{E}^*) \left[\frac{\partial g}{\partial t} \right], \quad (8)$$

and the second term is used to define a momentum relaxation time $\tau(\epsilon)$:

$$\left[\frac{\partial g}{\partial t} \right] = -\frac{g}{\tau}. \quad (9)$$

For optical phonons,

$$\frac{1}{\tau_{op}} = \frac{D^2 m_i m_l^{1/2}}{\sqrt{2} \pi \hbar^3 \rho \omega_0} [N_q (\epsilon + \hbar \omega_0)^{1/2} + (N_q + 1) (\epsilon - \hbar \omega_0)^{1/2}] \quad (10)$$

where

$\hbar \omega_0$ = optical phonon energy, ρ = density of Ge, and $N_q = \{e^{\hbar \omega_0 / kT} - 1\}^{-1}$ neglecting dispersion

The term involving $(\epsilon - \hbar \omega_0)$ is present only for $\epsilon > \hbar \omega_0$. The deformation potential constants used in this calculation are taken from Ref. [1] as gathered from experiments of several kinds. They are tabulated in Table 1 together with other relevant data. For acoustic deformation potential scattering, a single relaxation time exists when equipartition is obeyed [1], and can be written

$$\frac{1}{\tau_{ac}} = \frac{\sqrt{2} \Xi_1^2 (m_i^2 m_l)^{1/2} kT}{\pi \hbar^4 \rho u_l^2} \epsilon^{1/2}. \quad (11)$$

Figure 1 shows the momentum relaxation times due to optical and acoustic deformation

Table 1. Numerical values used in calculations

$m_i = 1.64 m_0$
$m_l = 0.082 m_0$
$\rho = 5.46 \text{ g/cc}$
$u_l = 5.4 \times 10^5 \text{ cm/sec}$
$D = 4 \times 10^8 \text{ eV/cm}$
$\Xi_0^2 = 900 (\text{eV})^2$
$\Xi_1^2 = 151 (\text{eV})^2$
$\hbar \omega_0 = k (430^\circ)$

potential scattering at 77°K. It is seen that $1/\tau_{ac}$ is always several times greater than $1/\tau_{op}$. For $\epsilon < \hbar \omega_0$, $1/\tau_{op}$ can certainly be neglected. For hot electrons (fields above about 1 kV/cm), the effect of τ_{op} is the same as multiplying $\tau_{ac}(\epsilon)$ by a constant factor. In this paper $1/\tau_{op}$ was not included, but this is not expected to affect any of the conclusions.

For energy relaxation terms we have

$$\begin{aligned} \left[\frac{\partial f_0}{\partial t} \right]_{op} &= \frac{D^2 m_i m_l^{1/2}}{\sqrt{2} \pi \hbar^3 \rho \omega_0} N_q [(\epsilon + \hbar \omega_0)^{1/2} \\ &\times \{e^{\hbar \omega_0 / kT} f_0(\epsilon + \hbar \omega_0) - f_0(\epsilon)\} + (\epsilon - \hbar \omega_0)^{1/2} \\ &\times \{f_0(\epsilon - \hbar \omega_0) - e^{\hbar \omega_0 / kT} f_0(\epsilon)\}] \end{aligned} \quad (12)$$

where the term involving $(\epsilon - \hbar \omega_0)$ is present only for $\epsilon > \hbar \omega_0$; and

$$\begin{aligned} \left[\frac{\partial f_0}{\partial t} \right]_{ac} &= \frac{4 \sqrt{2} \Xi_1^2 m_i^2 m_l^{1/2} \epsilon^{1/2}}{\pi \hbar^4 \rho} \\ &\times \left[\frac{\epsilon kT}{2} f_0'' + \left(\frac{\epsilon}{2} + kT \right) f_0' + f_0 \right] \end{aligned} \quad (13)$$

where the primes denote differentiation with respect to ϵ . Again energy non-equipartition has been neglected.

For electron energies below about $10 \hbar \omega_0$ the optical mode scattering determines the energy loss. Above that however, acoustic mode scattering takes over as the main source of energy loss [3].

After matching the coefficients of P_0 and P_1 upon substitution of (6) into (7), we obtain the coupled equations

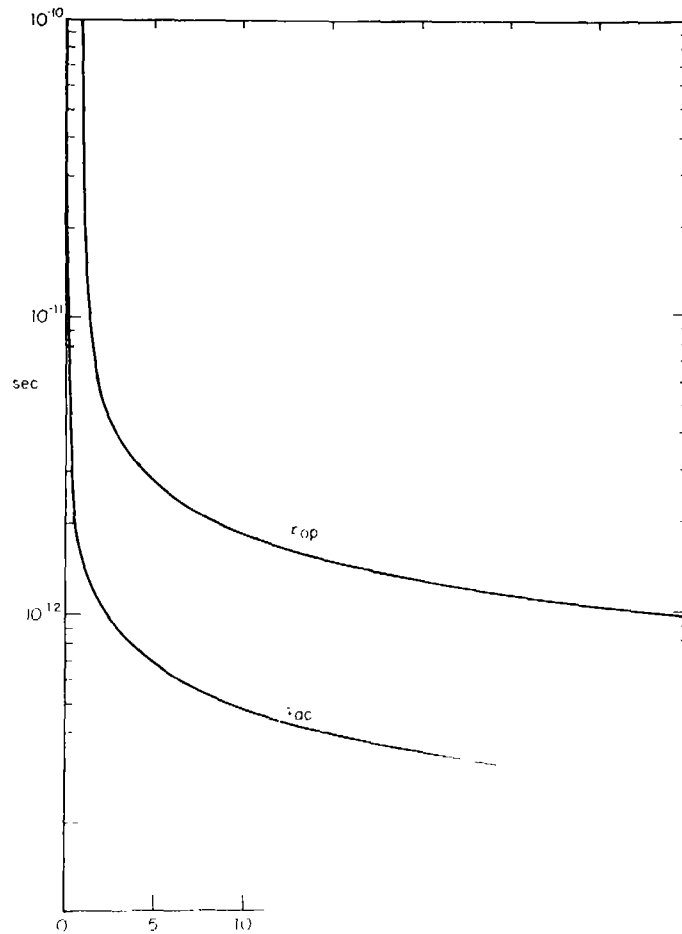


Fig. 1. Moment

$$-\frac{2}{3} \frac{eE^*}{\sqrt{2m_0\epsilon}} \frac{\partial}{\partial \epsilon} (\epsilon g(\epsilon)) + \left[\frac{\partial f_0}{\partial t} \right]_{op} + \left[\frac{\partial f_0}{\partial t} \right]_{ac} = 0 \quad (14)$$

$$-e \sqrt{\frac{2\epsilon}{m_0}} E^* \frac{\partial f_0}{\partial \epsilon} - \frac{g(\epsilon)}{\tau_{ac}} = 0. \quad (15)$$

Substituting $g(\epsilon)$ from (15) into (14) and changing to dimensionless variables such that ϵ is in units of $\hbar\omega_0$, and E^* is in units of kV/cm,[†] we get, numerically, for $\epsilon < 1$ and

[†]This will be the convention for the rest of this paper

$T = 77^\circ \text{K}$

$$\begin{aligned} & \left[\frac{\epsilon^2}{11.16} + 1.485\epsilon E^{*2} \right] \frac{\partial^2 f_0}{\partial \epsilon^2} + \left[\frac{\epsilon^2}{2} + \frac{1}{5.58\epsilon} \right. \\ & \left. + 1.485E^{*2} \right] \frac{\partial f_0}{\partial \epsilon} + \left[\epsilon - \frac{1}{48.2} \sqrt{\epsilon(\epsilon+1)} \right] f_0(\epsilon) \\ & + 5.38 \sqrt{\epsilon(\epsilon+1)} f_0(\epsilon+1) = 0 \end{aligned} \quad (16)$$

and for $\epsilon > 1$, $T = 77^\circ \text{K}$

$$\left[\frac{\epsilon^2}{11.16} + 1.485\epsilon E^{*2} \right] \frac{\partial^2 f_0}{\partial \epsilon^2} +$$

$$\begin{aligned}
& + \left[\frac{\epsilon^2}{2} + \frac{1}{5.58} \epsilon + 1.485 E^{*2} \right] \frac{\partial f_0}{\partial \epsilon} \\
& + \left[\epsilon - \frac{1}{48.2} \sqrt{\epsilon(\epsilon+1)} \right. \\
& \quad \left. - 5.38 \sqrt{\epsilon(\epsilon-1)} \right] f_0(\epsilon) + 5.38 \sqrt{\epsilon(\epsilon+1)} \\
& \times f_0(\epsilon+1) + \frac{1}{48.2} \sqrt{\epsilon(\epsilon-1)} f_0(\epsilon-1) = 0. \quad (17)
\end{aligned}$$

The drift velocity of electrons in the (100) direction is given by

$$\begin{aligned}
V_D &= \left(\sum_{\Delta k} \left(\frac{1}{\hbar} \nabla_{\Delta k} \epsilon \right) f(\Delta k) \right) \cdot \left\langle -\sqrt{\frac{2}{3}}, 0, \sqrt{\frac{1}{3}} \right\rangle \\
&= \left(\sum_{\Delta k} \frac{\hbar \Delta k^*}{m_0} f(\Delta k^*) \right) \cdot \frac{\mathbf{E}^*}{E} \\
&= \frac{1}{3} \sum_{|\Delta k^*|} \frac{\hbar |\Delta k^*|}{m_0} g(\epsilon) \frac{|\mathbf{E}^*|}{E} \\
&= \frac{\frac{1}{3} \int_0^\infty \sqrt{\frac{2\hbar\omega_0\epsilon}{m_0}} \sqrt{\epsilon} g(\epsilon) \frac{|\mathbf{E}^*|}{E} d\epsilon}{\int_0^\infty f_0(\epsilon) \sqrt{\epsilon} d\epsilon}. \quad (18)
\end{aligned}$$

The denominator in the last line of (18) is a normalizing constant for the distribution function. Upon substitution of (15) into (18) and evaluating numerically, we find

$$\begin{aligned}
|V_D| &= \frac{E^* \int_0^\infty f_0(\epsilon) d\epsilon}{\left(\frac{T}{77^\circ} \right) \int_0^\infty f_0(\epsilon) \sqrt{\epsilon} d\epsilon} \\
&\times 0.513 \times 10^7 \text{ cm/sec} \quad (19)
\end{aligned}$$

where $E^* = |\mathbf{E}^*| = 2.89 E$.

Equations (16) and (17) are to be solved for various values of E^* , and (19) is then used to find the field dependent drift velocity.

There are some simple consequences of (19). If we assume a Maxwellian distribution over the entire energy range having a temperature T_c , where T_c is in units of 77°K, then (19) gives

$$\begin{aligned}
|V_D| &= \frac{2E^*}{\sqrt{\pi}} \left(\frac{T_c}{5.58} \right)^{-1/2} \left(\frac{T}{77^\circ} \right)^{-1} \\
&\times 0.513 \times 10^7 \text{ cm/sec.} \quad (20)
\end{aligned}$$

If $T_c = T$, which is the case for very low fields, (20) predicts a $T^{-1.5}$ temperature dependence of the low field mobility. Equation (20) gives a low field mobility of 39,500 cm²/V-sec at 77°K. For higher temperatures the inclusion of optical phonon momentum relaxation becomes necessary and a departure of the low field mobility from a $T^{-1.5}$ temperature dependence results. Next, supposing that in the case of hot electrons the distribution functions should again be adequately represented by Maxwellians, with electron temperature T_c increasing as E^2 , then (20) predicts a field-independent drift velocity.

3. NUMERICAL SOLUTION

At $E^* = 0$, the solution is

$$f_0(\epsilon) = \text{const. } e^{-5.58\epsilon} \quad (21)$$

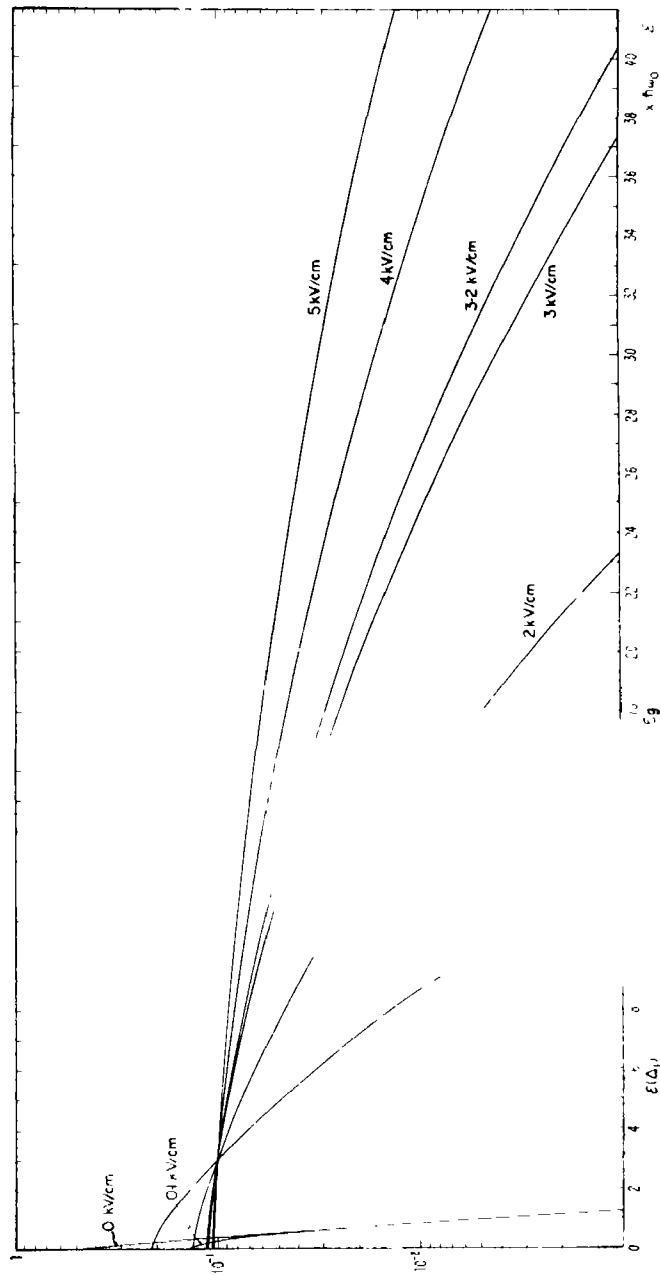
which is a Maxwellian at 77°K in our notation. For low fields, $f_0(\epsilon+1)$ differs from $f_0(\epsilon)$ by several orders of magnitude, so that it is not possible to expand $f_0(\epsilon+1)$ in a Taylor series about $f_0(\epsilon)$. A finite difference method is used as follows. Using

$$\frac{\partial f_0}{\partial \epsilon} \Big|_\epsilon = \frac{f_0|_{\epsilon+\Delta} - f_0|_{\epsilon-\Delta}}{2\Delta} \quad (22)$$

and

$$\frac{\partial^2 f_0}{\partial \epsilon^2} \Big|_\epsilon = \frac{f_0|_{\epsilon+\Delta} - 2f_0|_\epsilon + f_0|_{\epsilon-\Delta}}{\Delta^2} \quad (23)$$

we can write down a series of simultaneous equations for $f_0|_{-\Delta}, f_0|_0, \dots, f_0|_3$, arising from the evaluation of (16) and (17) at $\epsilon = 0, \Delta, \dots, 2$. There are about $1/\Delta$ to the nearest integer unknowns in excess of the number of equations. At low fields, all significant parts of the distribution function for $\epsilon \geq 2$ may be represented by a Maxwellian [2, 4]. This is justified, since for $\epsilon < 10$ acoustic energy relaxation may be neglected. Hence in order to solve the equations it was assumed that the distribution function was Maxwellian with some characteristic temperature T_c for all energies above



11) valleys in Ge (not normalized).

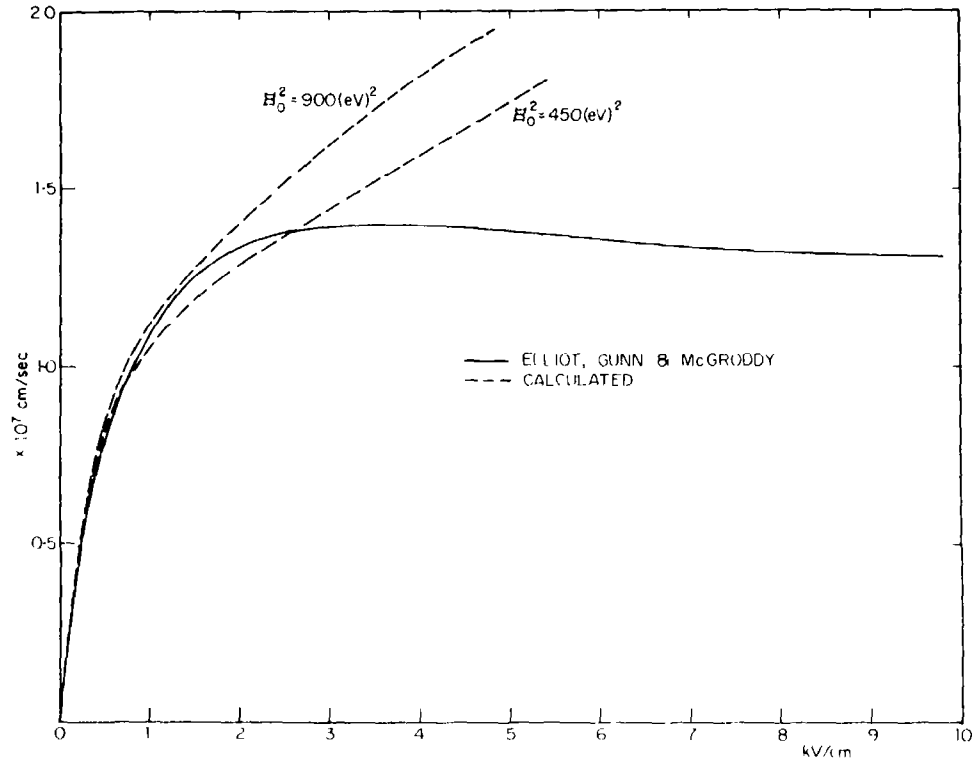


Fig. 3. Experimental and calculated drift velocity vs. field in *n*-GaAs.

$\epsilon = 2$. For each value of electric field, this temperature was determined by trying out different values of T_e until the correct analytic behavior of $f_0(\epsilon)$ near $\epsilon = 0$ was achieved[2]. The difference Δ was chosen to be 0.01, and thus a large number of simultaneous equations were generated. With the use of a large memory computer it was easy to solve the equations with all the standard precautions regarding overflow/underflow of coefficients. There was no difficulty in finding T_e to at least 3 significant places, since the behavior of the distribution functions near $\epsilon = 0$ was very sensitive to T_e . For higher fields (≥ 1 kV/cm) it is possible to expand $f_0(\epsilon + 1)$, and thus it is no longer necessary to assume the form of the distribution function over a unit energy interval. After determining the slope of the distribution function at $\epsilon = 3$ it is then possible to

continue integration of the differential equation up to energies such that the distribution function becomes insignificant.

The standard test for finite difference methods was used. The difference interval Δ was decreased (but not below such values that roundoff errors would occur), and a limiting form of solution was found. It was found, as expected[1, 2], that the electron temperature at $\epsilon = 3$ did increase as the square of the electric field. However the distribution functions obtained were not completely Maxwellian. Figure 2 presents the distribution functions obtained for various fields. The drift velocity did not saturate (Fig. 3), because the distribution functions fell off faster than Maxwellians for energies above $\epsilon = 10$. Thus fewer electrons get into the higher energy region where momentum loss is greater. The

whole calculation was repeated with acoustic phonon energy relaxation (Ξ_0^2) halved. It was found that the distribution functions did not differ from Maxwellians as much as they did as shown in Fig. 2. The 'Druyvestyn' type distribution function ($\propto e^{-\text{const } \epsilon^2}$) obtained at higher energies ($\epsilon > 10$) is thus due to acoustic phonon energy relaxation. The drift velocity-field curves obtained are shown in Fig. 3 together with the experimental curve of Elliot, Gunn and McGroddy[5].

4. DISCUSSION OF RESULTS

The chief conclusions to be drawn from this calculation are as follows. (1) The usual model of electron transport in the (111) valleys in Ge does not yield current saturation but a rather large positive differential conductivity at high fields, because of the effects of acoustic energy loss. This has in the past been noticed by Meyer and Jorgensen[6], but here a more quantitative feeling is given to this effect. Using the accepted parameters listed in Table 1, this model gives a form of drift velocity field curve in agreement with experiment only up to 2 kV/cm. (2) The optical deformation potential should not be inferred from the saturation drift velocity as given by Reel

Risken's theory. It can however be deduced from the quadratic conductivity at low fields as given in this model. (3) The distribution functions obtained in this model at high fields (> 2 kV/cm) are essentially Druyvestyn, rather than Maxwellian as assumed in Ref. [2]. (4) For fields of about 2 kV/cm and above, the distribution functions obtained indicate that the effects of higher minima need definitely to be considered, because of the large overlap of the distribution functions over energies greater than $\epsilon(\Delta_1)$.

Acknowledgements—The author wishes to thank Professor H. Brooks for his guidance, and is indebted to him for many discussions and a critical reading of the manuscript. He is also grateful to the Information Processing Center of the Massachusetts Institute of Technology for the use of its IBM 360/65 and other facilities.

REFERENCES

1. CONWELL E. M., *High Field Transport in Semiconductors*, Suppl. 9, *Solid State Physics*, Academic Press, New York (1967).
2. REIK H. G. and RISKEN H., *Phys. Rev.* **124**, 777 (1961) and **126**, 1737 (1962).
3. CONWELL E. M., *Phys. Rev.* **135**, A1138 (1964).
4. BUDD H., *Proc. Int. Conf. Phys. Semiconduct.*, Kyoto, p. 420 (1966).
5. ELLIOT B. J., GUNN I. B. and MCGRODDY I. C., *Phys. Rev.* **146**, 823 (1967).

OPTICAL ANISOTROPY OF $A^2B^4C_2^{5-}$ CRYSTALS

N. A. GORYUNOVA, I. B. ZLATKIN and E. K. IVANOV

Academy of Sciences of the USSR, A. F. Ioffe Physico-Technical Institute, Leningrad K-21, USSR

(Received 27 August 1969; in revised form 12 December 1969)

Abstract—The existence of synchronism directions in $CdGeP_2$ crystals has been revealed and the short wavelength synchronism boundary for $\lambda \approx 1.75 \mu$ ($h\nu \approx 0.7$ eV) has been determined from measurements of the indices of refraction of the ordinary n_o and extraordinary n_e beams.

The synchronism condition for $ZnSiP_2$, $CdSiP_2$ and $ZnGeP_2$ is satisfied in the crystal transmission region due to the large value of the birefringence $|\Delta n|$.

The value of the linear electrooptical effect r_{61} in $CdGeP_2$ has been estimated. In the crystal transmission region it was found that $r_{61} = 20 \times 10^{-8}$ in units CGSE.

We have found experimentally the dependence of the birefringence on the cation tetrahedral radii in $ZnSiP_2$, $CdSiP_2$, $ZnGeP_2$, $CdGeP_2$ crystals.

1. INTRODUCTION

IN RECENT years due to the progress in nonlinear optics, an interest in optically anisotropic materials with nonlinear polarizability has developed [1-3].

The investigations presented in this paper were spurred by the fact that in a number of $A^2B^4C_2^{5-}$ compounds the second harmonic generation has been found with ruby ¹ illumination [4].

If, in optically anisotropic materials, $A^2B^4C_2^{5-}$ crystals belonging to the point group $42m$, i.e. the same as for the condition

$$n_o^{2\nu} - n_e^{2\nu} > n_o^{2\nu} - n_o^\nu$$

where $n_o^{2\nu}$ and $n_e^{2\nu}$ are the indices of refraction of the ordinary and extraordinary beams respectively, at the frequency 2ν , and n_o^ν is the index of refraction of the ordinary beam at the frequency ν , is satisfied. There exists the synchronism direction, along which a significant increase of the second harmonic power can be obtained.

In this work from the measurements of indices of refraction of the ordinary n_o and extraordinary n_e beams, the existence of the synchronism directions in the $CdGeP_2$ crystals has been found and the short wave-

length synchronism boundary has been determined.

Apart from the application of $CdGeP_2$ to nonlinear optics, we have considered an effect connected with the display of the nonlinear properties in this crystal. The value of this linear electrooptical effect was estimated according to the measured n_o and n_e and the

2. EXPERIMENTAL RESULTS

For measurements of the refraction indices n_o and n_e and also for measurements of the maximum birefringence it was necessary to have crystals oriented about the optical axis C . Three orientation methods applied by us to different crystals are given below.

$ZnSiP_2$ and $CdSiP_2$ single crystals were produced by the vapour transport reaction technique and had the form of platelets and

¹ $ZnSiP_2$ and $CdSiP_2$ crystals have been grown by Yu. A. Valov, R. I. Plechko and E. N. Ushakova.

faced needles with well made face (112). It is known from X-ray investigations that the C axis in ZnSiP_2 and CdSiP_2 makes an angle of $\sim 35^\circ$ and $\sim 37^\circ$, respectively, with the (112) plane, according to the relation $\alpha = \arctg a\sqrt{2}/c$ (a and c are the lattice constants).

For this reason in transmitting light through crystals with $\mathbf{E} \parallel (112)$ we measured the birefringence Δn_ϕ of ZnSiP_2 and CdSiP_2 . The angle between $\mathbf{E}$ and C axis projection on (112) was equal to 45° (Fig. 1), since it was the

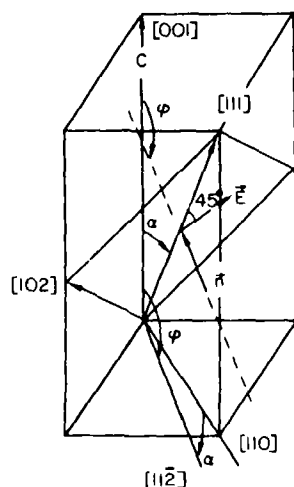


Fig. 1 Orientation of the plane-polarized light about C axis in ZnSiP_2 and CdSiP_2 crystals

best condition to observe the polarized light interference[5]. To calculate the maximum birefringence we used the relation[6]

$$\Delta n = \frac{\Delta n_c}{\sin^2 \varphi} \quad (2)$$

where φ is the angle between the wave normal $\mathbf{n}$ and the C axis direction.

CdGeP_2 has been produced* by the directed recrystallization technique in the form of unfaced single crystalline ingots, hence the crystal orientation method given above could not be used.

The CdGeP_2 crystal orientation about the C axis was carried out by the optical method. From the single crystalline ingot we cut out initially a platelet (1 in Fig. 2) arbitrarily

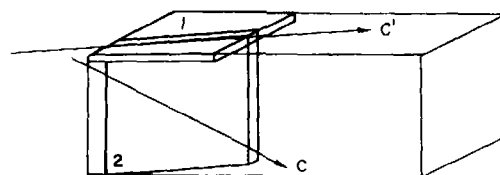


Fig. 2 The optical method of the CdGeP_2 crystal orientation about C axis.

oriented about the growth direction. Then the platelet was placed between parallel polaroids. By rotating the specimen and observing extinctions and clear spaces in passing light, we found the direction of the C axis projection C' on the specimen 1 plane and the direction perpendicular to it. The two mutually perpendicular directions could be distinguished due to the well pronounced dichroism of the CdGeP_2 crystals.

As is known from the theoretical calculations[7] and the experimental results of the chalcopyrite band structure investigations[8], the intensity of the light passing through the crystal is larger for $\mathbf{E} \parallel C$ than for $\mathbf{E} \perp C$ near the absorption edge. This gave us a means of determining the direction of the C axis projection. Thus, after we had determined the direction of the C axis projection C' on the platelet 1 plane, we cut the next platelet 2 in such a way that C' lay in the cut plane, the latter having been perpendicular to the platelet 1 plane. Therefore, in specimen 2 the C axis lay in the platelet plane (within an accuracy of $\pm 2^\circ$).

ZnGeP_2 single crystals have been produced† by the recrystallization from a small-crystalline powder by means of the vertical Bridgman technique. We could not use the CdGeP_2

* CdGeP_2 has been grown by A. S. Borschevski and Y. K. Undalov

† ZnGeP_2 has been grown by I. M. Ivanova and V. D. Prochukhan.

crystal orientation method for the ZnGeP₂ crystals since their weakly pronounced dichroism Q , which was probably due to impurities, did not permit determination of the direction of the C axis projection on the specimen plane and the direction perpendicular to it. For this reason we initially cut out from the single crystalline ingot a platelet oriented arbitrarily about the growth direction and measured Δn_φ for it. Then we cut out the platelet, whose plane was perpendicular to the first platelet plane, and measured $\Delta n_{\varphi+90^\circ}$ for it. From these values we could determine the angle between the C axis and the specimen plane and calculate the value of the maximum birefringence with the following relations:

$$\begin{aligned}\Delta n_\varphi &= \Delta n \sin^2 \varphi \\ \Delta n_{\varphi+90^\circ} &= \Delta n \cos^2 \varphi \\ \varphi &= \arctg \sqrt{\frac{\Delta n_\varphi}{\Delta n_{\varphi+90^\circ}}}.\end{aligned}\quad (3)$$

To determine n_o and n_e the interference from the planeparallel platelet at $\mathbf{E} \perp \mathbf{C}$ and $\mathbf{E} \parallel \mathbf{C}$ was observed. The n_o and n_e determination accuracy is ~ 5 per cent and is limited by the specimen thickness measurement accuracy case $d = (22 \pm 1) \mu$. We could measure n_e only for CdGeP₂.

To determine the birefringence, we observed the polarized light interference[5] on ZnSiP₂, CdSiP₂, ZnGeP₂ and CdGeP₂ crystals. The accuracy of the Δn measurement, which was determined by the device resolution, was no worse than 0.4 per cent since the minimum specimen thickness was $(363 \pm 1) \mu$.

3. EXISTENCE OF THE SYNCHRONISM DIRECTIONS AND APPLICATION PROMISE OF THE ELECTROOPTICAL EFFECT IN CdGeP₂

The refractive index values in the crystal transmission region at $h\nu = 1.2$ eV (Fig. 3), $n_o = 3.8$, and $n_e = 3.6$ are in a good agreement with the birefringence value $\Delta n = 0.18$ at $h\nu = 1.2$ eV (Fig. 4). At $h\nu = 0.4$ eV, $\Delta n = 0.11$. Consequently, in the photon energy range (1.7–0.4) eV CdGeP₂ crystal is negative, i.e. $n_o > n_e$. At $0.4 \text{ eV} \leq h\nu \leq 0.7 \text{ eV}$ condition (1) is realized indicating the existence of the synchronism directions in CdGeP₂.

It is more likely that the condition (1) is also fulfilled for the far i.r. region of the spectrum at $h\nu < 0.4$ eV and at the absence of the refraction index inversion. The synchronism condition (1) is not fulfilled at $h\nu > 0.7$ eV due

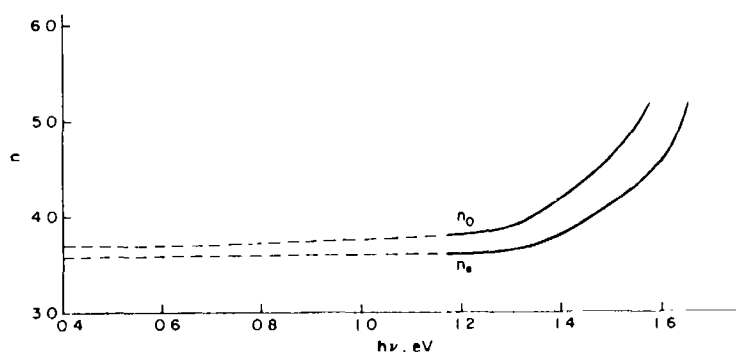


Fig. 3. The dependence of the refraction indices of the ordinary n_o and extraordinary n_e beams of CdGeP₂ crystal upon photon energy $h\nu$. — from measurements of the interference from a plane-parallel platelet --- from measurements of the birefringence Δn

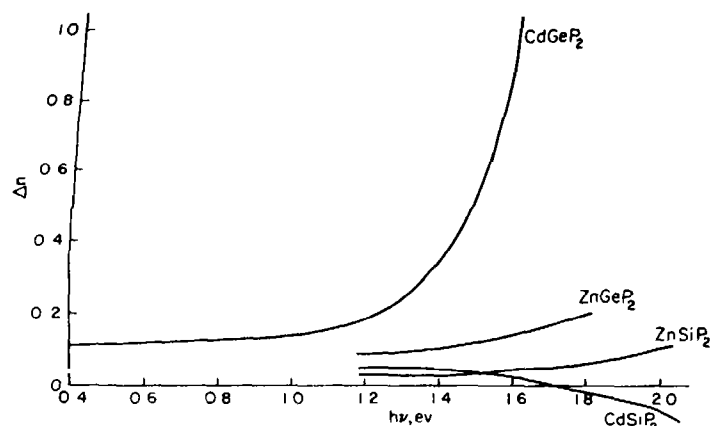


Fig. 4. The dependence of the birefringence of $A^2B^4C_2^5$ crystals upon photon energy $h\nu$.

also fulfilled in the crystal transmission region due to the large value of $|\Delta n|$.

The electrooptical effect is known to exist in crystals without the inversion center. If the ion mechanism does not participate in the process of second harmonic generation, then the elements of the linear electrooptical effect tensor τ_{ij} and that of the nonlinear susceptibility tensor χ_{ij} are related by the equation[9]

$$\tau_{ij} = -8\pi A_i \chi_{ij} \quad (4)$$

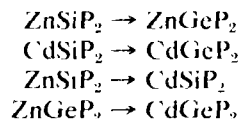
where $A_1 = a_1$, $A_2 = a_2^2$, ..., $A_6 = a_1 \cdot a_2$; $a_i = 1/n_i^2$ are polarization constants ($i = 1, 2, 3$).

To estimate τ_{ij} in $CdGeP_2$ at $\lambda = 1 \mu$ (i.e. in the crystal transmission region) we used the value χ_{14} measured in the vicinity of the main absorption edge[4] at $\lambda = 6943 \text{ \AA}$. Taking into account the dispersion of χ_{ij} near the absorption edge[1], we used for the crystal transmission region the value of χ_{14} from[4] decreased by a factor of five[†]. The electrooptical coefficient obtained in this way is $r_{41} = 40 \times 10^{-8}$ (units CGSE).

[†]For example, for GaAs the values of χ_{ij} in the absorption region (6943 Å) and in the transmission region (10.6 μ) differ by a factor of 2.5–5[3].

4. BIREFRINGENCE IN $A^2B^4C_2^5$ CRYSTALS

Measurements of $|\Delta n|$ in $ZnSiP_2$, $CdSiP_2$ and $CdGeP_2$ crystals revealed the following regularities. If the change of the absolute value of $|\Delta n|$ (Table 1) is considered, it is seen that in substituting for the first ($Zn \rightarrow Cd$) or for the second ($Si \rightarrow Ge$) cation in pairs of the compounds:



the birefringence value increases (Fig. 5) with increasing cation tetrahedral radius. The ion tetrahedral radii in $A^2B^4C_2^5$ compounds[10] are close to the tetrahedral radii calculated by Pauling. However, in substituting for the second cations $Si \rightarrow Ge$ in the pairs shown the

Table 1

Compound	Tetrahedral compression $2.00-c/a$	The birefringence value in the crystal transmission region $ \Delta n $ at $\lambda(\mu)$	
$ZnSiP_2$	0.07	0.03	1
$CdSiP_2$	0.16	0.05	1
$ZnGeP_2$	0.04	0.09	1
$CdGeP_2$	0.12	0.11	3

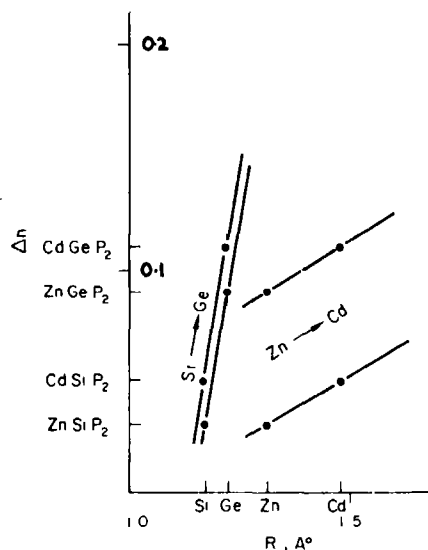


Fig. 5 The dependence of the birefringence of $A^2B^4C_2^5$ crystals on the tetrahedral radii R of cations of the second and fourth groups of the periodic system

change of $|\Delta n|$ is more pronounced than that for the first cations $Zn \rightarrow Cd$, even though the tetrahedral radii increase more considerably in substituting Zn for Cd than Si for Ge . The dependence of $|\Delta n|$ on the cation tetrahedral radii for phosphides of ternary compounds obeys the equation

$$|\Delta n| = K_1 R_1 + K_2 R_2 - A$$

where R_1 and R_2 are the tetrahedral radii of cations of the second and the fourth group, $K_1 = 0.118 \text{ \AA}^{-1}$, $K_2 = 1.2 \text{ \AA}^{-1}$, $A = 1.53$. The

difference in magnitudes of K_1 and K_2 reflected by different slopes of $|\Delta n| = f(R)$ curves, can be explained by the effect of the electron shell structure of atoms on the optical anisotropy of the crystals. The structures of electron shells of Zn and Cd are similar to each other and differ only in the main quantum number. The difference between Si and Ge atoms is more essential since Ge , unlike Si , has the filled up d -states. This is apparently one of the reasons why the birefringence increases more considerably in substituting Si for Ge in the pairs considered above than in substituting Zn for Cd .

Acknowledgements—The authors are grateful to E. F. Gross for his constant help in the work and helpful discussions, to V. D. Prochukhan for the discussion of the results and to the group of collaborators mentioned in the paper for the production of crystals for measurements

REFERENCES

1. BLOMBERGEN N., *Nelineynaya optika* Izd. Mir, Moscow (1966).
2. AKHMANOV S. A. and KHOKHLOV R. V., *Usp. fiz. Nauk*, **88**, 3, 439 (1966).
3. RFST S., *Usp. fiz. Nauk*, **93**, 4, 633 (1967).
4. GORYUNOV A., RYVKIN S. M., ISHMAN I. M., STUPIN E. O., G. P. and VAROSHEVSKI I. M., *Acta crystallogr.* **11**, 224 (1958).
5. PEISLER H., *Acta crystallogr.* **11**, 224 (1958).

GALVANOMAGNETIC EFFECTS OF HOT ELECTRONS IN *n*-TYPE GERMANIUM*

M. KRIECHBAUM

Institut für theoretische Physik der Universität A-8010 Graz, Austria

and

H. HEINRICH

Institut für Angewandte Physik der Universität A-1090 Vienna and Ludwig-Boltzmann-Institut
für Festkörperphysik, Vienna, Austria

(Received 12 September 1969)

Abstract— Numerical calculations of the magnetoconductivity of *n*-Ge in the $\langle 100 \rangle$ and $\langle 111 \rangle$ crystallographic directions were performed at 80°K and for field strength up to 5 kV/cm. It is shown that it is necessary to consider the dependence of the population of different valleys on the magnetic field in order to get agreement with experimental results.

1. INTRODUCTION

As it is well known, the conduction band of germanium exhibits 4 equivalent spheroidal energy minima oriented along the $\langle 111 \rangle$ -axes in *k*-space. An application of a high electric field results in heating of the electrons which may be different in each valley if the electric field does not point in a $\langle 100 \rangle$ direction. This difference of the mean energy of the electrons is responsible for the fact that there are more electrons in the lower energy valleys. The application of a transverse magnetic field has two effects on the carrier distribution: (1) it reduces their mobility and (2) the resulting Hall field causes a deviation of the electric field. Therefore, due to the mass anisotropy of the electrons the energy gain from the electric field is changed. This causes a repopulation of carriers depending on the magnetic field. In this way the galvanomagnetic behavior may be changed considerably.

A model following the ideas outlined above was developed recently by Heinrich and Kriechbaum[1] (hereafter referred to as I). It was assumed that the electrons in each

valley obey a Maxwellian energy distribution with a temperature which may be different in each valley. Then the mobility tensor is solved exactly in the magnetic field **B** according to the transport theory of Herring and Vogt[2]. For further references see I. The electron temperatures are determined by the method of energy balance. The number of electrons in each valley is determined by an

80°K which have been reported recently by Movchan[3].

2. NUMERICAL CALCULATIONS FOR *n*-Ge

The mobility in *n*-Ge at 80°K lattice temperature is mainly determined by acoustical, optical, and intervalley phonon scattering and ionized impurity scattering. Influences of the higher conduction band minima along the $\langle 100 \rangle$ axis are not taken into account, and therefore the results derived in the following are applicable as long as population of the upper valleys is not appreciable. The

*Work supported by 'Fonds zur Förderung der wissenschaftlichen Forschung' Austria

acoustic relaxation times are given in Ref. [2] and are:

$$\frac{1}{\tau_1} = A \left[1.31 \left(\frac{\Xi_d}{\Xi_u} \right)^2 + 1.61 \frac{\Xi_d}{\Xi_u} + 1.01 \right] \quad (1a)$$

$$\frac{1}{\tau_{\parallel}} = A \left[1.24 \left(\frac{\Xi_d}{\Xi_u} \right)^2 + 2.32 \frac{\Xi_d}{\Xi_u} + 1.22 \right] \quad (1b)$$

with A given by equation (1, 6). The optical and intervalley relaxation times are given by equations (1, 7) and (1, 14) and by Conwell [4] equation (3.6.11). For ionized impurity scattering the relaxation times are given by Eagles and Edwards [5] as

$$[C \ln(4D^{-1})] \tau_{\parallel} = 40.4 \quad (2a)$$

$$[C \ln(4D^{-1})] \tau_{\perp} = 3.61 \quad (2b)$$

with C and D defined in equation (1, 8).

As in I, the energy loss for acoustic, intervalley, and optical phonon scattering and the particle number in the different valleys were calculated. The parameters used for the calculations are summarized in Table 1. The results for the transverse magnetoconductivity with $\mathbf{j} \parallel [111]$ and $\mathbf{B} \parallel [1\bar{1}0]$ are shown in Fig. 1 for $B = 4$ kG and 6 kG, and $n = 10^{15} \text{ cm}^{-3}$. The dots and triangles are experimental points by Movchan [3] for $n = 10^{15} \text{ cm}^{-3}$ and $n = 4 \cdot 10^{14} \text{ cm}^{-3}$ respectively, obtained at a magnetic field-strength of 6 kG. Unfortunately, no absolute values are given in that paper. We therefore normalized them arbitrarily to the calculated Ohmic values. Also included in the figure is the calculated Ohmic value of the magnetoconductivity for $n = 4 \cdot 10^{14} \text{ cm}^{-3}$. The experimental results show a stronger dependence on carrier concentration than the theoretical ones. It can be seen that the model is able to explain the unusual magneto-resistance behavior qualitatively, that is, a region of negative magnetoresistance.

For $B = 0$ and $\mathbf{j} \parallel [111]$ two different types of valleys are present. The valley on the $[111]$ axis has the lower effective mobility

Table 1. Parameters used in the numerical calculations. The data are taken from Ref. [2] if not stated otherwise

Effective mass ratio	m_i/m_0	1.58
Dielectric constant	κ	0.082
Density (g/cm ³)	ρ	16§
Elastic constants (dyn/cm ²)	c_{11}	5.35
	c_{12}	1.573×10^{12}
	c_{44}	0.53×10^{12}
	c^*	0.680×10^{12}
Deformation potential constants (eV)	Ξ_d	-0.534×10^{12}
Coupling constants	Ξ_u	-9.07^*
	D_{np}	19.3*
	(eV/cm)	$4 \times 10^{*†}$
	D_n	1.02†
	(eV)	
Characteristic phonon temperatures (°K)	T_{op}	430§
	T_{ir}	280

*Ref. [4] page 170, Ref [263]

†Ref [4] page 171, Ref [264].

‡Ref [7] page 100, Ref [100].

§Ref. [4] page 133.

$E\mu\mathbf{E}/E^2$, $\mathbf{E}$ being the electric field and μ being the mobility tensor. Therefore, the electrons in this valley remain cooler than in the other minima and their number exceeds the Ohmic value. After application of a magnetic field pointing in the $[1\bar{1}0]$ direction three differently heated valleys are present (the valleys $[1\bar{1}1]$ and $[\bar{1}11]$ have the same electron temperatures). The Hall field points in the $[11\bar{2}]$ direction so that the electrons in the $[111]$ valley can take up more energy from the field. The temperature in this valley raises therefore and electrons are transferred to the other valleys. As one may expect from the particular arrangement of the conduction band minima in k -space the difference in electron temperature of the valleys on the $[\bar{1}\bar{1}1]$ and the $[1\bar{1}1]$ axes is small compared to the difference between the temperatures of the valleys on the $[111]$ and $[1\bar{1}1]$ axes. The relative changes in occupation number of the $[111]$ valley for different magnetic fields are shown in Fig. 1.

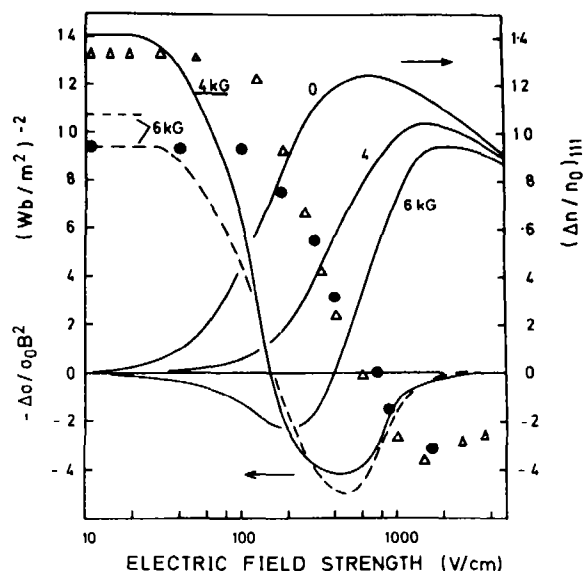


Fig. 1. Calculated magnetoconductivity vs. electric field strength at 80°K lattice temperature for $\mathbf{j} \parallel [111]$ and $\mathbf{B} \parallel [1\bar{1}0]$ for 4 and 6 kG and a carrier concentration of $n = 10^{15} \text{ cm}^{-3}$. The dash-dotted curve indicates the Ohmic value for $n = 4 \cdot 10^{15} \text{ cm}^{-3}$. The solid dots are experimental values for $n = 10^{15} \text{ cm}^{-3}$ and the triangles for $n = 4 \cdot 10^{15} \text{ cm}^{-3}$ and $B = 6 \text{ kG}$, taken from Ref. [3]. They are normalized to the theoretical Ohmic values for $n = 10^{15} \text{ cm}^{-3}$. Also included are the theoretical values for the valley on the

For 6 kG and low electric fields the population of the $[1\bar{1}1]$ valley is lower than in the Ohmic case. The reason for this can be seen from Fig. 2. The Hall field has about the same magnitude as the externally applied field so that the total electric field points in the $[22\bar{1}]$ direction. The energy gain in the $[111]$ valley is therefore higher than in the $[1\bar{1}1]$ valley contrarily to the case when no magnetic field is present. The influence of the Hall field can also be seen in Fig. 3, where the ratios of the electron temperature of the $[111]$ valley to the lattice temperature and of the $[1\bar{1}1]$ valley to that on the $[1\bar{1}1]$ axis are shown. For small electric fields the temperature of the $[1\bar{1}1]$ valley is lower than in the $[111]$ valley if a magnetic field of 6 kG is applied.

For $B \neq 0$ there are two types of valleys. Fig. 4 shows also the relative change of the occupation number of the $[111]$ -valley to its equilibrium number which is equal to that of the $[1\bar{1}1]$ valley. For comparison experimental values of Movchan[3] are indicated in Fig. 4. As in case of Fig. 1 they are normalized to the theoretical Ohmic values for $n = 10^{15} \text{ cm}^{-3}$.

*The measuring technique used to obtain these values was essentially the same as described in (1). The samples had an electron concentration of $4 \times 10^{15} \text{ cm}^{-3}$ and dimensions of about $1 \times 1 \times 7 \text{ mm}^3$. Contacts were prepared by As-diffusion and Ni-plating.

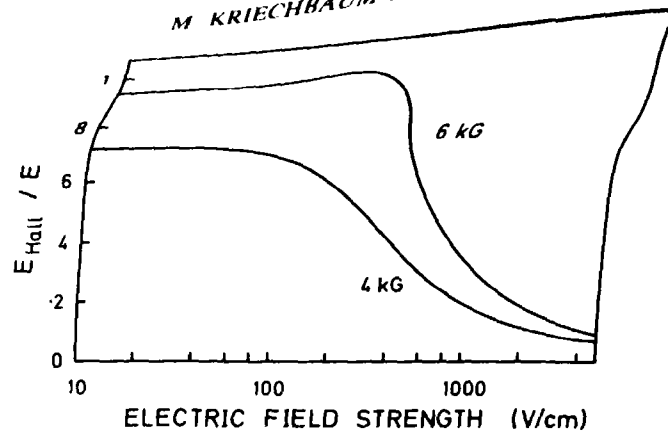


Fig. 2. Ratio of Hall field to electric field vs. electric field strength for $j \parallel [111]$ and $B \parallel [1\bar{1}0]$. Lattice temperature is 80°K.

malized to the theoretical Ohmic values. In this configuration both experimental and theoretical values exhibit only a positive magnetoresistance.

3. DISCUSSION

It has been shown that the model is able to explain qualitatively the negative transverse magnetoresistance. In the following we discuss the validity of the assumptions made in the calculations. For electric field strengths

up to 2000 V/cm the electron temperatures raises in the cooler valley to 350°K and in the hotter to 1700°K as can be seen in Fig. 3. According to the criterion of Fröhlich and Paranjape[6], equation (1, 1), the minimum carrier concentration for establishing a Maxwellian distribution at 600°K is 10^{15} cm^{-3} . As shown in Fig. 1 most of the carriers at 2000 V/cm are in the valley on the $[111]$ axis and the current is mainly determined by the mobility in this valley. It is therefore

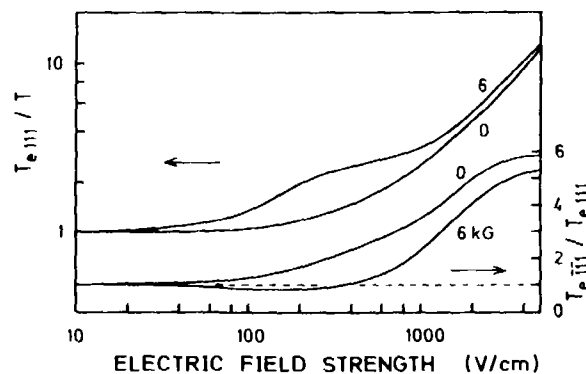


Fig. 3. Ratio of electron temperature of the $[111]$ valley to lattice temperature 80°K, and ratio of electron temperatures of two different valleys ($T_{e[111]}/T_{e[111]}$) vs. electric field strength for $j \parallel [111]$ and $B \parallel [1\bar{1}0]$. The dashed curve indicates where these two temperatures are equal.

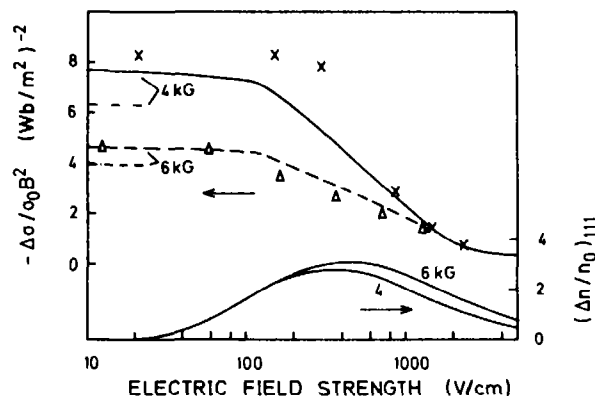


Fig. 4. Calculated magnetoconductivity vs. electric field strength at 80°K for $j \parallel [100]$ and $B \parallel [010]$ for 4 and 6 kG and a carrier concentration of $n = 4 \cdot 10^{14} \text{ cm}^{-3}$. The dash-dotted curves indicate the Ohmic values for $n = 10^{15} \text{ cm}^{-3}$. The crosses are experimental values for $B = 4 \text{ kG}$ and $n = 4 \cdot 10^{14}$. The triangles are experimental values taken from ref. [3] for $n = 4 \cdot 10^{14} \text{ cm}^{-3}$ and $B = 6 \text{ kG}$. They are normalized to the theoretical Ohmic values. Included is the theoretical relative change in electron population of the valley on the [111]-axis for $n = 4 \cdot 10^{14} \text{ cm}^{-3}$.

justified to use a Maxwellian distribution for samples with a carrier concentration of 10^{15} cm^{-3} or larger. As in I we neglected the energy exchange between electrons of different valleys due to intervalley scattering processes in the energy-balance equation again this contribution is small compared to the energy exchange with the lattice. We conclude that the negative transverse magnetoresistance may only be explained if the dependence of the electron distribution among different valleys on the magnetic field is taken into account.

Acknowledgements—It is a pleasure to thank Professors Dr. K. Baumann and Dr. K. Seeger for helpful dis-

cussions and Dr. H. Preier for a critical reading of the manuscript. Thanks are due also to the Institut für Statistik der Universität, Vienna, for making available their computer.

REFERENCES

6. FROHICH H. and PARANJAPPI D. S., *Proc. Roy. Soc. Lond.* **B69**, 21 (1956).
7. PAIGE F. G. S., *Progress in Semiconductors*, Vol. 8, Heywood, London (1964).

THE CRYSTAL STRUCTURE OF V_2O_3 AND $(V_{0.962}Cr_{0.038})_2O_3$ NEAR THE METAL-INSULATOR TRANSITION

P. D. DERNIER

Bell Telephone Laboratories, Incorporated, Murray Hill, N.J. 07974, U.S.A.

(Received 10 September 1969)

Abstract—The substitution of Cr^{3+} in the V_2O_3 lattice results in a Mott metal-insulator transition at room temperature with no change in space group symmetry. Structural refinements of single crystals of V_2O_3 and $(V_{0.962}Cr_{0.038})_2O_3$, by X-ray diffraction techniques show an increase in the short vanadium-vanadium distances at the transition, while the vanadium-oxygen distances remain essentially unchanged. The vanadium-vanadium distance across the shared octahedral face increases from 2.697 ± 0.001 Å to 2.746 ± 0.001 Å and the vanadium-vanadium distance across the shared octahedral edge increases from 2.882 ± 0.001 Å to 2.918 ± 0.001 Å when proceeding from pure V_2O_3 to the Cr^{3+} doped crystals.

1. INTRODUCTION

BECAUSE of its metallic conductivity and high hexagonal c/a ratio at room temperature, V_2O_3 stands apart from the other isostructural oxides Al_2O_3 , Fe_2O_3 , $\alpha\text{-Ga}_2O_3$, Ti_2O_3 , Cr_2O_3 , In_2O_3 , Tl_2O_3 , and Rh_2O_3 . The substitution of approximately 1 per cent Cr^{3+} in V_2O_3 causes a sharp drop in c/a from 2.83 to 2.78 while the electrical resistivity increases several orders of magnitude[1, 2]. The ratio then decreases smoothly down to a value of 2.74 as the chromium content increases from 1 to 100 per cent. When Cr^{3+} doping of pure V_2O_3 causes an increase in electrical resistivity, the application of pressure on the same sample causes a first order transition at 10 kbar which is accompanied by a decrease in electrical resistivity of several orders of magnitude[3]. This metal-insulator transition appears to be an example of a Mott transition in which the electrons localize on the ionic sites but no change in crystal symmetry occurs[4]. In order to determine the changes in interatomic distances associated with this transition, the crystal structure of V_2O_3 and $(V_{0.962}Cr_{0.038})_2O_3$ have been refined.

¹Quenched high pressure modification[6].

²Quenched high pressure modifications[5].

2. EXPERIMENTAL

The intensity measurements of both V_2O_3 and $(V_{0.962}Cr_{0.038})_2O_3$ single crystals were taken with a paper tape controlled, fully automatic, General Electric XRD-5 X-ray diffractometer. An 8° take-off angle was used along with a scintillation counter, decade scalar, and single Zr-filtered MoK radiation. The intensities were obtained by use of

spheres of radii 0.016 and 0.011 cm, respectively. The orientations of these spheres in the same order, were such that the $[\bar{1}10]$ and $[110]$ zones were parallel to the φ axis of the goniostat. It was expected that these orientations would tend to minimize the intrinsic multiple diffraction effects[7].

All reflections in the upper hemisphere of reciprocal space in the region $2\theta \leq 90^\circ$ were measured by peak-height technique[8]. A standard reflection was also monitored so as to keep a running check on crystal orienta-

tion. The total number of observed independent reflections for V_2O_3 was 203 and for the Cr^{+3} doped specimen, 216. Before the final refinement 15 reflections for pure V_2O_3 and 8 for the doped crystal were eliminated because of background errors and/or ≥ 20 per cent secondary extinction correction[9]. In sequential fashion the intensities of equivalent reflections were first averaged and then corrections for the Lorentz, polarization, and spherical absorption effects were applied [10, 11].

The final refinement procedure was identical for each crystal. The scattering factors, f , used were for neutral atoms and the $\Delta f'$ and $\Delta f''$ values were for Mo $K\alpha$ radiation [12, 13]. In the case of the 3.8 mole per cent substituted crystal, weighted averages were calculated for the f values. No adjustments were necessary for $\Delta f'$ and $\Delta f''$. The starting values for the positional parameters were those reported by Newnham and de Haan [14]. The first trial refinement was carried out by a least-squares program with the capability of refining the secondary extinction parameter C [15]. All observed independent reflections were used. The positional parameters, iso-

tropic temperature factors, scale factor, and C were refined simultaneously. Anisotropic temperature factors were introduced before the last twelve refinement cycles were carried out by the program ORFELS [16].

3. RESULTS

For the pure and doped samples respectively the statistical residual or R value, $(\sum |F_{obs} - F_{calc}| / \sum |F_{obs}|)$, was 0.019 and 0.020 with isotropic temperature factors, whereas it was 0.018 and 0.019 with anisotropic temperature factors. The actual function being minimized in both programs was $\sum w(|F_{obs}| - |F_{calc}|)^2$. The weighted R values, for the final anisotropic refinements were 0.025 and 0.030 respectively. The final parameters are listed in Table 1. In addition, a list of observed and calculated scattering amplitudes can be found in Table 4.

The lattice parameters for the two compounds, reported in Table 1, were obtained by measuring 2θ values for at least 10 reflections in the back-reflection region of powder photographs taken at room temperature with a Norelco camera of 114.6 mm dia. utilizing $CrK\alpha$ radiation ($K\alpha = 2.29092 \text{ \AA}$, $K\alpha_1 -$

Table 1. Crystallographic data for V_2O_3 and $(V_{0.962}Cr_{0.038})_2O_3$

Parameters	V_2O_3		$(V_{0.962}Cr_{0.038})_2O_3$	
	V	O	V-Cr	O
x	0.0	0.31164 $\pm$ 0.00018	0.0	0.30745 $\pm$ 0.00022
y	0.0	0.0	0.0	0.0
z	0.34630 $\pm$ 0.00002	0.25	0.34870 $\pm$ 0.00002	0.25
β_{11}	0.00545 $\pm$ 0.00025	0.00584 $\pm$ 0.00028	0.00540 $\pm$ 0.00024	0.00685 $\pm$ 0.00027
β_{22}	0.00545 $\pm$ 0.00025	0.00659 $\pm$ 0.00035	0.00540 $\pm$ 0.00024	0.00693 $\pm$ 0.00036
β_{33}	0.00031 $\pm$ 0.00002	0.00035 $\pm$ 0.00003	0.00034 $\pm$ 0.00002	0.00054 $\pm$ 0.00003
β_{12}	0.00272 $\pm$ 0.00012	0.00329 $\pm$ 0.00017	0.00270 $\pm$ 0.00012	0.00346 $\pm$ 0.00018
β_{13}	0.0	0.00018 $\pm$ 0.00004	0.0	0.00027 $\pm$ 0.00004
β_{23}	0.0	0.00037 $\pm$ 0.00008	0.0	0.00054 $\pm$ 0.00008
unweighted R	0.018		0.019	
weighted R	0.025		0.030	
a_H	4.9515 $\pm$ 0.0003 $\text{\AA}$		4.9985 $\pm$ 0.0005 $\text{\AA}$	
c_H	14.003 $\pm$ 0.001 $\text{\AA}$		13.912 $\pm$ 0.001 $\text{\AA}$	
c/a	2.8281		2.7832	
Sphere radius	0.0116 cm		0.017 cm	
μR	1.526		1.631	
Scale factor	1.427 $\pm$ 0.010		1.324 $\pm$ 0.009	
sec. extinction coefficient	0.47 $\times 10^{-4}$ $\pm$ 0.9 $\times 10^{-5}$		0.30 $\times 10^{-4}$ $\pm$ 0.28 $\times 10^{-5}$	

2.28962 Å). The refinement of the parameters was carried out with a least-squares program of Mueller, Heaton and Miller [17]. The appropriate final parameters listed in Table 1 were input to the program ORFFE which calculated the interatomic distances and bond angles reported in Table 2 as well as the root-mean-square thermal displacements and orientations in Table 3 [18]. Equivalent interatomic

distances and bond angles for Ti_2O_3 , Cr_2O_3 and $\alpha\text{Ga}_2\text{O}_3$ have been included in Table 2 for comparative purposes.

4. DISCUSSION

Both V_2O_3 and $(\text{V}_{0.962}\text{Cr}_{0.038})_2\text{O}_3$ are isostructural with $\alpha\text{Al}_2\text{O}_3$, space group $R\bar{3}c$, with approximate hexagonal close-packing of the oxygens and the cations occupying $\frac{2}{3}$ of

Table 2. Interatomic distances (Å) and bond angles (deg)

	Ti_2O_3 (Newnham and de Haan)	V_2O_3 (Current work) ^a	$(\text{V}_{0.962}\text{Cr}_{0.038})_2\text{O}_3$	Cr_2O_3 (Newnham and de Haan)	$\alpha\text{Ga}_2\text{O}_3$ (Marengo)
M^1-O^1	2.08	2.050 ± 0.001	2.062 ± 0.001	2.02	2.077
M^1-O^2	2.01	1.970 ± 0.001	1.975 ± 0.001	1.97	1.921
O^1-O^2	2.80	2.805 ± 0.001	2.791 ± 0.001	2.74	2.716
O^1-O^3	2.83	2.675 ± 0.002	2.664 ± 0.002	2.63	2.630
O^1-O^4	2.88	2.891 ± 0.001	2.895 ± 0.001	2.85	2.833
O^2-O^3	3.05	2.955 ± 0.001	3.004 ± 0.001	2.99	3.007
M^1-M^2	2.59	2.697 ± 0.001	2.746 ± 0.001	2.65	2.835
M^1-M^3	2.99	2.882 ± 0.001	2.918 ± 0.001	2.89	2.938
M^1-M^4	3.56	3.472 ± 0.001	3.451 ± 0.001	3.43	3.313
M^2-M^3	3.74	3.691 ± 0.000	3.702 ± 0.000	3.65	3.645
$O^1-M^1-O^2$	86.3	88.45 ± 0.01	87.46 ± 0.01	86.9	85.5
$O^1-M^1-O^3$	85.4	81.49 ± 0.03	80.49 ± 0.03	81.4	78.6
$O^2-M^1-O^3$		91.93 ± 0.02	91.63 ± 0.02		90.2
$O^2-M^1-O^4$	170.5	168.61 ± 0.03	168.61 ± 0.03	168.0	65.0
$O^3-M^1-O^4$	98.4	97.17 ± 0.03			
$M^1-O^1-M^2$	76.9	82.25 ± 0.01			
$M^1-O^2-M^2$	93.7	91.55 ± 0.01			
$M^1-O^3-M^2$	124.2	123.58 ± 0.01			
$M^1-O^4-M^2$	132.0	133.24 ± 0.01			

^a Standard deviations have been rounded. Step was equivalent to adding the error from σ .

Table 3. R.m.s. Thermal displacements (Å) and orientation angles of component of thermal displacement along principal axis (R) in Angstroms (Å)

	V			O			V-Cr			O		
1	0.065 ± 0.002			0.064 ± 0.003			0.069 ± 0.002			0.069 ± 0.003		
2	0.067 ± 0.001			0.068 ± 0.002			0.072 ± 0.001			0.076 ± 0.002		
3	0.067 ± 0.002			0.080 ± 0.002			0.072 ± 0.001			0.090 ± 0.002		
	Angle between principal axis (<i>R</i>) and x, y, z											
	V			O			V-Cr			O		
<i>R</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
1	90.0	90.0	0.0	90.0	58.1	142.5	90.0	90.0	0.0	90.0	46.1	126.8
2	0.0	120.0	90.0	0.0	120.0	90.0	0.0	120.0	90.0	0.0	120.0	90.0
3	120.0	0.0	90.0	90.0	133.4	127.5	120.0	0.0	90.0	90.0	121.3	143.2

Table 4. Observed and calculated structure factors for V_2O_3

H	K	L	F _O	F _C	H	K	L	F _O	F _C	H	K	L	F _O	F _C	H	K	L	F _O	F _C	H	K	L	F _O	F _C	
0	0	-18	22.1	21.2	-1	5	15	19.2	19.4	-3	1	-13	7.3	8.1	-4	8	15	11.5	12.1	-6	-3	0	75.2	74.9	
0	1	14	66.1	62.5	-1	6	-8	14.6	12.6	-3	-2	-5	9.6	9.9	-4	9	5	10.3	10.1	-6	4	8	11.7	11.2	
0	1	20	75.3	75.5	-1	6	-8	14.9	14.7	-3	-2	-7	7.9	9.3	-5	0	9	65.1	69.2	-6	4	11	7.9	8.7	
0	1	26	62.2	62.9	-1	6	-16	70.2	70.7	-3	-3	10	117.2	119.9	-5	0	10	77.4	76.4	-6	4	-16	69.5	67.0	
0	2	16	93.4	97.4	-1	6	-19	9.2	8.8	-3	-2	14	55.6	54.7	-5	0	-20	52.7	54.0	-6	6	-6	54.5	51.4	
0	2	20	63.3	67.9	-1	7	-14	33.8	34.9	-3	-2	16	91.5	90.2	-5	0	22	37.9	37.5	-6	8	-5	11.0	10.4	
0	3	12	93.6	96.1	-1	7	15	54.2	55.4	-3	-3	18	11.0	11.1	-5	-1	2	27.3	26.7	-7	0	-4	40.6	39.8	
0	3	4	61.2	61.3	-2	-1	2	59.3	57.8	-3	-4	18	50.8	50.4	-5	-2	0	22.2	22.0	-7	-2	-16	44.7	44.4	
0	4	-10	109.3	113.0	-2	-1	-9	51.3	50.9	-3	-4	14	49.4	47.6	-5	-2	-10	84.3	86.2	-7	-1	4	52.2	51.4	
0	4	14	43.4	41.2	-2	-1	14	62.3	60.3	-3	-5	13	7.8	7.1	-5	-2	11	7.8	7.4	-7	-2	-2	22.0	22.7	
0	5	-4	27.0	26.4	-2	-1	-18	24.5	23.4	-3	-6	6	57.8	56.7	-5	-3	16	81.1	82.1	-7	-2	-8	8.1	7.6	
0	5	-14	51.1	51.4	-2	-1	20	68.6	66.8	-3	-6	12	66.8	67.2	-5	-3	-20	57.3	60.7	-7	-2	12	31.3	29.9	
0	5	16	39.4	37.6	-2	-1	27	15.6	16.4	-3	-7	2	42.2	42.5	-5	-4	-7	11.1	10.3	-7	-2	18	14.4	13.8	
0	6	12	59.2	59.6	-2	-2	9	31.8	34.0	-3	-7	14	31.3	29.8	-5	-4	-9	25.2	25.4	-7	-4	10	82.7	83.8	
0	6	22	33.6	39.3	-2	-2	12	43.2	40.5	-3	-7	16	53.3	57.6	-5	-4	11	9.1	9.0	-7	-8	0	59.9	58.9	
0	7	8	21.9	21.3	-2	-2	14	67.8	66.8	-3	-10	16	56.4	55.5	-5	-4	21	15.2	15.6	-7	-8	1	12.5	12.3	
0	7	-10	75.3	75.8	-2	-2	-18	21.0	20.1	-3	-10	18	68.9	68.7	-5	-6	1	13.4	13.8	-7	-9	-7	7.9	7.5	
0	7	14	25.2	25.4	-2	-2	-21	17.9	17.9	-3	-10	20	70.3	72.8	-5	-6	4	73.6	75.2	-8	-1	9	11.6	11.4	
0	8	4	53.6	54.8	-2	-2	22	50.9	51.7	-4	-1	1	9.2	9.3	-5	-6	-5	12.6	12.7	-8	-1	-12	27.8	27.5	
0	-1	-22	58.6	57.3	-2	-2	26	64.0	65.0	-4	-1	-8	23.4	23.1	-5	-6	10	72.6	73.3	-8	-3	2	18.5	17.5	
0	-1	20	9.9	9.1	-2	-2	3	43.7	46.6	-4	-1	-20	68.4	68.5	-5	-6	13	10.1	10.6	-8	-4	1	41.0	42.2	
0	-1	-24	36.6	37.1	-2	-2	4	10	82.0	-4	-2	-5	10.4	10.9	-5	-6	-14	47.9	46.5	-8	-4	-6	69.7	69.8	
0	1	2	5	14.0	13.6	-2	-2	4	15	24.0	-4	-2	2	11.7	11.0	-5	-7	-9	15.3	15.9	-8	-4	9	15.0	13.9
0	1	-2	7	12.3	12.5	-2	-2	4	-24	33.0	-4	-2	19	8.6	7.8	-6	-0	0	105.9	109.7	-8	-4	-12	30.1	30.7
0	1	-12	50.5	50.5	-2	-2	5	-10	10.3	-4	-2	3	21.1	21.1	-6	-0	18	9.2	9.2	-8	-5	-1	61.7	61.7	
0	1	-25	30.2	30.1	-2	-2	5	2	32.8	-4	-2	5	54.9	55.9	-6	-1	11	11.0	10.6	-8	-5	16	62.0	62.5	
0	1	26	61.0	62.1	-2	-2	5	-3	18.4	-4	-4	-3	15.0	15.2	-6	-1	17	6.8	6.5	-8	-6	-11	9.9	9.3	
0	1	3	4	90.7	92.8	-2	-2	5	-4	93.7	-4	-4	4	79.5	78.7	-6	-1	20	50.5	50.2	-8	-6	13	9.8	9.1
0	1	3	10	112.4	113.8	-2	-2	5	-15	13.8	-4	-4	-8	27.4	27.4	-6	-2	1	11.5	12.1	-8	-7	-6	63.2	62.5
0	1	3	11	8.1	10.7	-2	-2	5	-1	11.2	-4	-4	-8	27.4	27.4	-6	-2	1	11.5	12.1	-8	-7	-6	63.2	62.5
0	1	3	16	77.3	75.7	-2	-2	6	-4	59.3	-4	-5	2	96.2	98.1	-6	-2	4	70.6	72.7	-9	-2	1	8.1	7.5
0	1	-22	52.0	51.4	-2	-2	6	-14	44.5	-4	-5	2	19.6	16.5	-6	-2	-7	10.1	10.2	-9	-2	4	44.0	46.9	
0	1	-4	2	53.4	60.8	-2	-2	7	6	78.8	-4	-5	-4	50.9	50.4	-6	-2	-10	55.2	56.5	-9	-3	6	42.1	44.5
0	1	-4	2	53.4	60.8	-2	-2	7	6	78.7	-4	-5	-4	50.9	50.4	-6	-2	-10	55.2	56.5	-9	-3	6	42.1	44.5
0	1	4	-6	103.8	110.4	-2	-2	7	16.3	16.6	-4	-5	13	9.6	9.3	-6	-2	-20	55.3	55.7	-9	-4	10	55.8	56.1
0	1	4	12	37.6	36.4	-3	-1	-1	17.2	16.5	-4	-6	17	7.7	6.7	-6	-3	0	123.2	132.3	-9	-9	1	11.3	11.0
0	1	4	18	17.9	17.1	-3	-1	8	16.2	14.8	-4	-8	0	66.5	65.5										

Observed and calculated structure factors for $(V_{0.962}Cr_{0.038})_2O_3$

H	K	L	F0	FC	H	K	L	F0	FC	H	K	L	F0	FC	H	K	L	F0	FC	H	K	L	F0	FC		
0	0	12	108.3	101.7	-1	6	-19	9.7	9.7	-3	-3	6	75.0	63.8	5	0	-10	78.0	78.2	6	-4	16	60.9	61.4		
0	0	18	45.2	43.7	-1	6	-20	52.0	54.6	-3	-3	6	37.1	36.1	5	0	14	63.8	63.2	6	-5	-4	28.9	80.8		
0	0	-24	27.6	26.8	-1	9	2	12.5	11.7	-3	-3	4	2	58.9	5	1	1	15.5	16.2	-6	-5	-14	58.0	58.8		
0	0	2	8	31.6	28.1	-1	9	2	12.5	11.7	-3	-3	4	2	58.9	5	1	11	11.8	12.0	-6	-5	6	50.6	50.7	
0	0	2	10	130.3	125.9	-1	16	53.8	55.6	-3	-3	2	6.9	11.2	5	-2	1	11.8	13.5	-6	-7	-7	6.3	6.1		
0	0	2	16	91.8	89.8	-1	2	-9	29.9	32.1	-3	-5	-9	10.4	10.3	5	-2	-6	23.7	26.2	-6	-8	0	56.0	55.2	
0	0	3	24	25.3	26.3	-1	2	14	85.4	83.5	-3	-5	10	56.7	57.7	5	-2	-10	86.1	87.6	-6	-9	6	41.2	41.5	
0	0	10	116.3	117.8	-1	2	22	30.9	30.0	-3	-5	13	5.2	5.6	5	-3	-4	60.6	64.9	-6	-9	4	40.6	41.0		
0	0	5	16	70.8	71.7	-1	2	24	48.2	49.9	-3	-5	16	74.6	75.4	5	-3	5	12.0	12.1	-7	-0	8	31.8	31.3	
0	0	5	22	21.3	21.4	-1	2	-26	57.4	58.2	-3	-5	22	24.3	23.7	5	-3	5	7.4	6.9	-7	-0	10	79.2	79.5	
0	0	6	0	104.8	107.8	-1	3	1	19.8	19.9	-3	-5	22	55.3	51.9	5	-3	11	7.5	6.1	-7	-0	16	37.2	38.2	
0	0	8	4	54.6	54.3	-1	3	10	123.2	122.1	-3	-5	24	43.1	43.1	5	-3	20	60.7	61.4	-7	-1	0	62.5	61.8	
0	0	8	4	10.6	9.8	-1	3	14	77.4	76.2	-3	-5	24	43.1	43.1	5	-3	20	60.7	61.4	-7	-1	0	62.5	61.8	
0	0	10	158.5	152.6	-1	3	-20	23.9	23.0	-3	-5	24	43.1	43.1	5	-3	20	60.7	61.4	-7	-1	0	62.5	61.8		
-1	-1	-10	53.5	48.5	-1	3	-20	23.9	23.0	-3	-5	24	43.1	43.1	5	-3	20	60.7	61.4	-7	-1	0	62.5	61.8		
-1	-1	-14	83.6	79.2	-1	3	-20	23.9	23.0	-3	-5	24	43.1	43.1	5	-3	20	60.7	61.4	-7	-1	0	62.5	61.8		
-1	-1	1	16	87.8	83.7	-1	4	3	40.6	44.8	-3	-5	24	43.1	43.1	5	-3	20	60.7	61.4	-7	-1	0	62.5	61.8	
-1	-1	1	22	39.4	37.4	-1	4	-15	21.3	21.7	-3	-5	24	43.1	43.1	5	-3	20	60.7	61.4	-7	-1	0	62.5	61.8	
-1	-1	1	-26	54.6	55.9	-1	4	-21	16.1	15.7	-3	-5	24	43.1	43.1	5	-3	20	60.7	61.4	-7	-1	0	62.5	61.8	
-1	-1	2	5	16.1	16.2	-1	4	-21	16.1	15.7	-3	-5	24	43.1	43.1	5	-3	20	60.7	61.4	-7	-1	0	62.5	61.8	
-1	-1	2	6	185.6	187.7	-1	4	-21	16.1	15.7	-3	-5	24	43.1	43.1	5	-3	20	60.7	61.4	-7	-1	0	62.5	61.8	
-1	-1	2	9	43.7	45.5	-1	4	-21	16.1	15.7	-3	-5	24	43.1	43.1	5	-3	20	60.7	61.4	-7	-1	0	62.5	61.8	
-1	-1	-12	30.6	27.8	-1	4	-21	16.1	15.7	-3	-5	24	43.1	43.1	5	-3	20	60.7	61.4	-7	-1	0	62.5	61.8		
-1	-1	2	17	6.8	6.1	-1	4	-21	16.1	15.7	-3	-5	24	43.1	43.1	5	-3	20	60.7	61.4	-7	-1	0	62.5	61.8	
-1	-1	2	19	33.9	31.9	-1	4	-21	16.1	15.7	-3	-5	24	43.1	43.1	5	-3	20	60.7	61.4	-7	-1	0	62.5	61.8	
-1	-1	2	22	17.9	14.1	-1	4	-21	16.1	15.7	-3	-5	24	43.1	43.1	5	-3	20	60.7	61.4	-7	-1	0	62.5	61.8	
-1	-1	3	2	53.0	51.9	-1	4	-26	6.8	10.1	9.0	4	-4	4	50.9	80.9	6	0	-12	22.3	22.9	8	-1	9	9.5	9.4
-1	-1	3	-4	135.3	137.9	-1	4	-26	6.8	10.1	9.0	4	-4	4	50.9	80.9	6	0	-12	22.3	22.9	8	-1	9	9.5	9.4
-1	-1	3	13	6.7	6.2	-1	4	-26	6.8	10.1	9.0	4	-4	4	50.9	80.9	6	0	-12	22.3	22.9	8	-1	9	9.5	9.4
-1	-1	3	13	9.1	9.4	-1	4	-26	6.8	10.1	9.0	4	-4	4	50.9	80.9	6	0	-12	22.3	22.9	8	-1	9	9.5	9.4
-1	-1	3	16	82.2	81.8	-1	4	-26	6.8	10.1	9.0	4	-4	4	50.9	80.9	6	0	-12	22.3	22.9	8	-1	9	9.5	9.4
-1	-1	4	3	26.7	29.6	-1	4	-26	6.8	10.1	9.0	4	-4	4	50.9	80.9	6	0	-12	22.3	22.9	8	-1	9	9.5	9.4
-1	-1	4	8	35.4	38.4	-1	4	-26	6.8	10.1	9.0	4	-4	4	50.9	80.9	6	0	-12	22.3	22.9	8	-1	9	9.5	9.4
-1	-1	4	10	114.7	117.3	-1	4	-26	6.8	10.1	9.0	4	-4	4	50.9	80.9	6	0	-12	22.3	22.9	8	-1	9	9.5	9.4
-1	-1	5	0	93.5	100.9	-1	4	-26	6.8	10.1	9.0	4	-4	4	50.9	80.9	6	0	-12	22.3	22.9	8	-1	9	9.5	9.4
-1	-1	5	6	99.9	104.7	-1	4	-26	6.8	10.1	9.0	4	-4	4	50.9	80.9	6	0	-12	22.3	22.9	8	-1	9	9.5	9.4
-1	-1	6	1	6.5	6.1	-1	4	-26	6.8	10.1	9.0	4	-4	4	50.9	80.9	6	0	-12	22.3	22.9	8	-1	9	9.5	9.4
-1	-1	6	2	14.8	14.8	-1	4	-26	6.8	10.1	9.0	4	-4	4	50.9	80.9	6	0	-12	22.3	22.9	8	-1	9	9.5	9.4

striking effect of the Cr substitution is the unexpected expansion in the M^I-M^{II} interatomic distance across the shared octahedral face from 2.697 to 2.746 Å. (See Fig. 1 and Table 2). This occurs despite the contraction of the c_H lattice parameter and the substitution of Cr^{+3} , an ion of smaller radius than V^{+3} . In addition to this, the interatomic distance M^I-M^{III} across the shared octahedral edge increases from 2.882 to 2.918 Å or approximately 1.2 per cent which is comparable to the 1 per cent expansion in the a_H parameter when proceeding from pure V_2O_3 to the Cr doped sample. Also in keeping with these increases in cationic distances, the unit cell volume of the Cr doped sample is 1.5 per cent larger than pure V_2O_3 .

It seems plausible to attribute the distortion of the oxygen octahedra to the increase in the vanadium-vanadium distances. In order to maintain reasonable cation-anion distances the oxygens of the unshared octa-

hedral face expand their interatomic distances, $O^{II}-O^{VI}$, from 2.955 to 3.004 Å, whereas those of the shared octahedral face, O^I-O^{III} , contract from 2.675 to 2.664 Å. At the same time the distance between the parallel, shared and unshared octahedral faces decreases from 2.334 to 2.319 Å (see Fig. 2). The umbrella-like distortion of the oxygen octahedron allows both the M^I-M^{II} and M^I-M^{III} distances to increase while maintaining essentially fixed cation-anion distances. In addition this mechanism explains the rather dramatic decrease in the c_H parameter from 14.003 to 13.912 Å, and the expansion in the a_H parameter from 4.9515 to 4.9985 Å. Also, one could expect from a simple view of a Mott transition that both vanadium-vanadium distances would necessarily expand resulting in a localization of electrons when proceeding from metal to insulator. This is in complete agreement with the actual distortion observed when comparing pure V_2O_3 to $(\text{V}_{0.962}\text{Cr}_{0.038})_2\text{O}_3$.

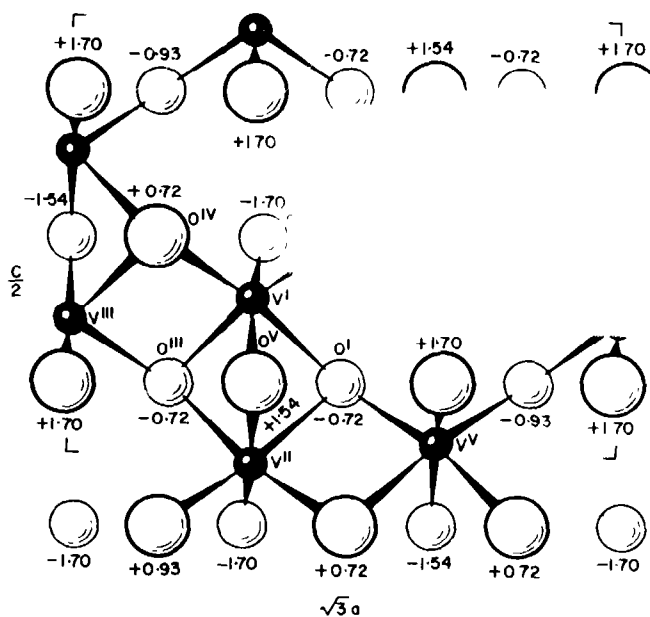


Fig. 1. A projection of the V_2O_3 structure on a plane perpendicular to the $[110]$ axis. The V atoms are at zero height and the heights of the oxygens are given in angstroms above and below the plane of projection.

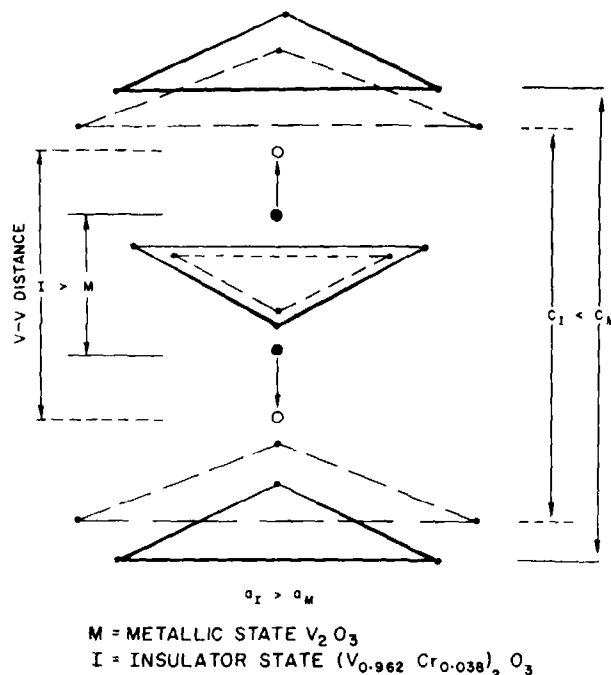


Fig. 2 An illustration of the 'umbrella-like' distortion of the oxygen octahedra in V_2O_3 due to the Cr^{+3} substitution and the expansion in the vanadium-vanadium distance across the shared octahedral face

The thermal motion of the oxygen atoms in both the pure and doped samples shows a distinctly anisotropic character, which in most respects agrees well with the proposed distortion mechanism. For example, in Table 3, the r.m.s. thermal displacements of the cations are nearly identical reflecting the unchanged cation-anion distances. On the other hand, the oxygen displacements are somewhat different. The larger vibrational displacements of the oxygens in the Cr doped sample are indicative of the increased oxygen-oxygen distances of the unshared octahedral face.

It has been observed that V_2O_3 is unique among the α -corundum oxides with respect to the M^I-M^{III} distance across the shared octahedral edge. This metal-metal distance was shown to be anomalously short for V_2O_3 in a plot of M^I-M^{III} vs. the effective ionic

radii of M [5]. In fact, V_2O_3 is the only member of the series to achieve this while maintaining a high c/a ratio. The M^I-M^{III} distance in the Cr doped sample is not anomalously short. Nor is this the case for pure Cr_2O_3 . However for all three crystals the M^I-M^{III} distance across the shared octahedral face remains anomalously short. This strongly suggests that the short M^I-M^{III} distance in V_2O_3 at room temperature is associated with its metallic properties.

From Table 2 and Fig. 1 it is clear that the interatomic angles, metal-oxygen-metal, are markedly different for metallic V_2O_3 than the rest of the isostructural series. In particular the bond angle $M^I-O^{III}-M^{III}$ across the shared octahedral edge is 1° smaller than the same angle in the Cr^{+3} doped specimen and 2° smaller than the equivalent angle for the rest of the members. Also the M^I-O^I-M

angle across the shared octahedral face is smaller than the Cr doped equivalent and smaller than the others with the exception of Ti_2O_3 . As it is known that the band structures of the transition metal oxides are strongly dependent on hybridization effects between the metal and oxygen atoms [19], one could argue that these interatomic angles are as significant as the short metal-metal distances in determining the metallic character of V_2O_3 .

5. CONCLUSION

It has been observed that the Mott transition in the Cr_2O_3 - V_2O_3 system, in which the conduction electrons localize on their ionic sites, is accompanied by a discontinuous expansion in unit cell volume and decrease in c/a at room temperature. The distortion of the structure can be attributed to the fact that all the nearest neighbor V-V distances increase while the V-O distances remain unchanged. Finally, the anomalously short V-V distance across the shared edge of the oxygen octahedron in pure V_2O_3 is clearly associated with its metallic properties.

Acknowledgements—The author thanks A. S. Cooper for the lattice parameter determinations and R. C. Eubank for assistance with critical programming problems. The author is particularly indebted to J. P. Remick for excellent crystals and to M. Marezio and D. B. McWhan for many valuable discussions and continued interest in this work.

REFERENCES

1. NEWNHAM R. F. and de HAAN Y. M., *Progress Rep. No. XXVI*, Lab. Insulation Research, p. 11, Massachusetts Institute of Technology (1960).
2. MacMILLAN A. J., *Tech. Rep. No. 172*, Lab. Insulation Research, Massachusetts Institute of Technology (1962).
3. McWHAN D. B., RICE T. M. and REMFKA J. P., *Phys. Rev. Lett.* **23**, 1384 (1969).
4. MOTT N. F., *Proc. R. Phys. Soc.* **62**, 416 (1949).
5. PREWITT C. T. and SHANNON R. D., *Trans. Am. crystallogr. Ass.* **5**, 56 (1969).
6. MAREZIO M. and REMFKA J. P., *J. chem. Phys.* **46**, 1862 (1967).
7. ZACHARIASEN W. H., *Acta crystallogr.* **18**, 705 (1965).
8. MAREZIO M., REMFKA J. P. and DEFRNIER P. D., *Acta crystallogr.* **B25**, 955 (1969).
9. ZACHARIASEN W. H., *Acta crystallogr.* **16**, 1139 (1963).
10. FULTON R. C., (1968), Unpublished crystallographic computer program X-RAY (Fortran IV) Bell Telephone Laboratories.
11. FULTON R. C., (1969), Unpublished crystallographic computer program SØRI (Fortran IV) Bell Telephone Laboratories.
12. CROMER F. E. and WABER J. F., *Acta crystallogr.* **18**, 104 (1965).
13. CROMER F. E., *Acta crystallogr.* **18**, 17 (1965).
14. NEWNHAM R. F. and de HAAN Y. M., *Z. Kristallogr.* **117**, 235 (1962).
15. PREWITT C. T., Unpublished least-squares refinement program (Fortran IV) F. T. Du Pont.
16. BUSING W. R., MARTIN K. O. and LEVY H. A., *ORNL Rep. TM 305* (1962).

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TECHNICAL NOTES

Non-stoichiometric defects in sapphire

(Received 21 August 1969; in revised form 4 May 1970)

A RECENT investigation of the literature by the author has indicated that the defect structure of sapphire is somewhat in doubt. Pappis and Kingery[1] investigated the variation of the electrical conductivity and thermoelectric power with oxygen pressure and temperature above 870°K and concluded that sapphire equilibrates with the atmosphere above this temperature. They proposed that aluminum vacancies are formed in high oxygen pressure (1 atm) and either interstitial aluminum ions or oxygen vacancies were formed in low oxygen pressure ($< 10^{-5}$ atm). Their four probe technique, however, while showing that contact resistances to platinum were small, is very susceptible to conduction along the surface and through the gas phase. In fact, the activation energies they found at the highest temperatures, 5.5-5.8 eV are very close to that found by Loup and Anthony[2] for phase conduction (5.7 eV). In addition Tallan *et al.*[3,4] have shown that in sapphire there exists a region which extends from the surface into the specimen as much as 1 mm and whose conductance changes rapidly with distance from the atmosphere. Thus Pappis and Kingery's results may reflect the changes in this region, in the surface, and in the gas phase, with changing atmosphere and temperature.

With this in mind the author has initiated a study of the defect structure of sapphire at high temperatures and its equilibration with the atmosphere. The technique employed is to heat treat disk shaped specimens 1mm thick by 10mm dia. in high and low oxygen pressures at a temperature of 2070°K, and to quench in any defect structure induced by such treatments. The conductivity of the quenched specimens is then measured at

much lower temperatures, by a three terminal technique, there being both electronic guarding and physical guarding to eliminate conduction along the surface, through any sub-surface layer and through the gas phase. A polarization technique[5] was employed to separate the ionic from the electronic conduction processes where at all possible. Details of the quench rate, and measurement technique will be available in forthcoming paper. The quench rate was, however, at least 100°K/min.

Figure 1 shows the preliminary results of the conductivity measurements for two specimens, one heat treated in an oxygen pressure of 1 atm for 4 hr (i.e. 'oxidized') the other in a vacuum giving an oxygen pressure of at most 10^{-8} atm, for 4 hr (i.e. 'reduced'). Because of the extremely low electronic conductivity of the reduced specimen compared to the oxidized specimen, its ionic conductivity could not be determined. It

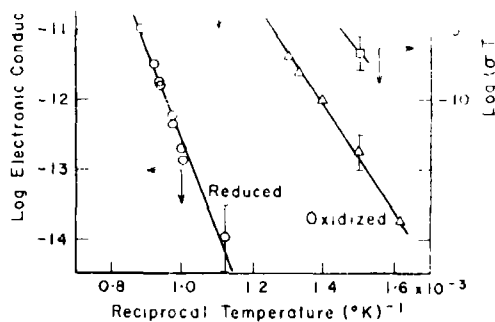


Fig. 1 Conductivities of heat treated sapphire specimens.

should be noted that for the ionic conductivity of the oxidized specimen, the product σT is plotted against $1/T$. The activation energies for the three conductivities are 1.5 ± 0.03 , 2.6 ± 0.5 , and 1.2 ± 0.3 eV for the electronic conductivity of the oxidized specimen, the reduced specimen, and the ionic conductivity of the oxidized specimens, respectively.

There would thus appear to be some difference in the electronic conductivities due to the different heat treatments. There are several possible explanations. Different impurity levels between the specimens could explain the differences noted. The specimens, however, came from the same boule, and care was taken to avoid impurity pickup from the furnace. The specimens were analyzed by a mass spectrographic technique for transition metal ions. These are the most likely impurities to be picked up. Table I shows the results of this analysis. Tantalum and tungsten were

to point to the atmosphere having a strong effect. Thus, intrinsic defects can be eliminated. Variations in the quench rate permit another possible explanation. If there was any variation it was the reduced specimen which had the faster quench rate which would imply that more defects would be quenched in, contrary to the conductivity evidence. Possible electronic trapping effects were eliminated also by measuring the electronic conductivity after irradiation with X-rays. No change was detected.

It would thus appear that none of the above explanations is likely, and that the difference in atmosphere between the two specimens is the predominating factor. It is proposed therefore that at least partial equilibration of the bulk of sapphire has occurred. Further, it is tentatively suggested that defects are created in the bulk of sapphire when heated above 2000°K in an oxygen pressure of 1 atm. From the present evidence, no defect structure can be suggested for the reduced specimen. The most probable defects which can be created in a high oxygen pressure are aluminum vacancies. Associates of these defects with impurity ions such as the iron shown in Table I can also occur, but the present evidence is not sufficient to separate these two possibilities. However, the existence of associates implies a sufficient concentration of aluminum vacancies to form the associates, so the following argument is not negated by their creation. Only the mechanisms and the defects will be different. Aluminum vacancies will be created according to the reaction.

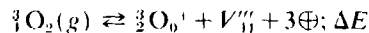
Table I. Mass spectrographical analysis of sapphire specimens

Elements	Sample no. 4*	Sample no. 9*
Li	ND - 5	ND - 5
V	ND - 5	ND - 5
Cr	ND - 1	ND - 1
Mn	ND - 1	ND - 1
Fe	20	20
Co	ND - 10	ND - 10
Ni	ND - 5	ND - 5
Cu	20	20
Ta	ND - 1000	ND - 1000
W	ND - 500	ND - 500

* Concentrations in ppm

ND - not detectable

also included since the vacuum heating elements were tungsten, while the heat shields were tantalum. No significant difference in impurity levels is apparent. Intrinsic Schottky-Wagner or Frenkel defects can also be formed and quenched in. These defects, however, depend solely on temperature for their creation, and the evidence seems



where Kroger's notation[6] has been employed. ΔE is the energy for the reaction. Fully ionized vacancies are shown in the reaction (1) but their ionization state at lower temperatures is uncertain, since Kroger has shown from his galvanic cell[7] data that the assump-

tion of the normal valence for intrinsic defects is not necessarily true below 1400°K. Thus the source of the activation energy for electronic conduction in the oxidized specimen could be the ionization energy from one of the lower ionization states to a higher one.

Further evidence for the creation of aluminum vacancies comes from the activation energy of the ionic conductivity of the oxidized specimen. The diffusion data of Kingery *et al.*[8,9], admittedly in polycrystalline alumina, has been interpreted as giving an energy for the motion of aluminum ions of 0.91 ± 1.0 eV. The similarity between this value and that found for the ionic conductivity, 1.2 eV, thus appears to verify that aluminum vacancies exist at the lower temperatures, and predominate in the ionic conduction mechanism.

If the above argument holds, then, on assuming a reasonable value for the hole mobility of $1.0 \text{ cm}^2/\text{Vsec}$, the concentration of the quenched in vacancies, N_v , which act as acceptor sites may be determined from the standard relation for conductivity. Taking $\sigma = 10^{-9} (\Omega \text{ cm})^{-1}$ at 1000°K, one finds that $N_v \sim 10^{17} \text{ cm}^{-3}$ which is of the same magnitude as the claimed concentration of impurities. This concentration of quenched aluminum vacancies implies a deviation from stoichiometry at 2070°K of 1 part in 10^5 during the heat treatment. Vest[10] has concluded from the lack of thermogravimetric data over a wide range of temperatures and oxygen pressures that if there is any deviation from stoichiometry it is less than 3 parts in 10^5 . Since his maximum temperature was however, 1870°K, it is thus possible that a concentration of non-stoichiometric aluminum vacancies of 10^{17} cm^{-3} is created at the higher temperature of 2070°K.

Thus the present work indicates at least partial equilibration of the bulk of sapphire with the environment at temperatures above 2000°K. Non-stoichiometric aluminium vacancies are postulated as being the pre-

dominant defect at these temperatures in high oxygen pressures.

ITT Research Institute,
Chicago
Ill. 60616
U.S.A.

J. J. MILLIS

REFERENCES

1. PAPPIS J. and KINGERY W. D., *J. Am. Ceram. Soc.* **44**, (9) 459 (1961).
2. LOUP J. P. and ANTHONY A. M., *Rev. hautes Temp. & Refrac.* **1**, (3) 193 (1964).
3. TALLAN N. M. and DEWILLER D. P., *J. appl. Phys.* **34**, (6) 1650 (1963).
4. TALLAN N. M. and GRAHAM H. C., *J. Am. Ceram. Soc.* **48**, (10) 512 (1965).
5. VEST R. W. and TALLAN N. M., *J. appl. Phys.* **36**, (2) 543 (1965).
6. KROGER F. A., 'Chemistry of Imperfect Crystals', Interscience Publishers New York (1964).
7. KROGER F. A. *Proc. Brit. Ceram. Soc.* **1**, 167 (1964).
8. OISHI Y. and KINGERY W. D., *J. chem. Phys.* **33**, (2) 480 (1960).
9. PALADINO A. F. and KINGERY W. D., *J. chem. Phys.* **37**, (3) 957 (1962).
10. VEST R. W., Private Communications.

Contributions to Solid State Physics, Vol. 31, pp. 2579-2581.

investigating numerous crystal structures. In some cases, the symmetry has been C_{4h} , C_{6h} , or cubic symmetry in which the gadolinium ion was surrounded by eight anions such as in CaF_2 . In some cases the spectrum of gadolinium was investigated in a six-coordinated compound such as in CaO and in SrO . In these crystal hosts with six surrounding oxy-

*Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

gen ions it was found that the cubic field was small, smaller than in the eight-coordinated compounds. It is, therefore, of interest to investigate the spectrum of Gd^{3+} with other ligands in octahedral coordination. The compound Cs_2ZrCl_6 is convenient for this purpose since rare earth ions easily replace the Zr ion, and the rare earth ions are surrounded by six Cl^- ions.

The spin Hamiltonian for a $S_{7/2}$ ion in a cubic field is

$$\mathcal{H} = \beta g S \cdot H + B_4^0 O_4^0 + B_4^4 O_4^4 + B_6^0 O_6^0 + B_6^4 O_6^4 = A S \cdot I \quad (1)$$

where the O_n^m , properly normalized, are operators which transform, as the spherical harmonics Y_n^m ; B_n^m are coefficients dependent upon the crystal field, which are to be determined by experiment; S is the electronic spin operator with $S = 7/2$ and I is the nuclear spin operator. Gd^{3+} has two unpaired isotopes

of nearly equal abundance, 15 per cent, and nuclear magnetic moment, both having $I = \frac{7}{2}$. Therefore, there are seven allowed electronic transitions ($\Delta M = \pm 1$), and each one must split into two unresolved sets of four allowed hyperfine lines ($\Delta m = 0$).

The spectra were measured at Q band and X band. The spectrum could be represented by a cubic spin Hamiltonian. The charge compensation, as often found for S state ions, must be far away. Only the central line $|+\frac{1}{2}\rangle \rightleftharpoons |-\frac{1}{2}\rangle$ was flanked by the hyperfine lines. The other lines apparently were too wide and the hyperfine structure was not completely resolved. The coefficients of the spin Hamiltonian were calculated from the Hamiltonian by first order perturbation theory, using equations 2 and 3 along the $[100]$ direction.

$$H_{1/2} = H_0 = \frac{h\nu}{g\beta}$$

$$H_{\pm 3/2} = H_0 \mp (-12b_4^0 + 14b_6^0)$$

$$H_{\pm 5/2} = H_0 \mp (-10b_4^0 - 14b_6^0)$$

$$H_{\pm 7/2} = H_0 \mp (20b_4^0 + 6b_6^0) \quad (2)$$

$$B_4^0 = \frac{1}{60} b_4^0$$

$$B_4^4 = \frac{1}{12} b_4^4 = \frac{1}{12} b_4^0$$

$$B_6^0 = \frac{1}{1260} b_6^0$$

$$B_6^4 = \frac{1}{60} b_6^4 = -\frac{1}{60} b_6^0 \quad (3)$$

Table 1. Measured and calculated Gd^{3+} of $\Delta M = \pm 1$ lines

Q band		X band	
H exp. ± 3 G	H calc	H exp. ± 0.5 G	H calc
12815	12817.5	3805.5	3804.3
12672	12670.5	3659.9	3658.5
12613	12613.5	3599.8	3599.0
12423	12423.0	3407.4	3409.2
12235	12232.5	3220.0	3219.3
12174	12175.5	3158.0	3159.8
12032	12028.5	3015.2	3014.0

The magnetic field in $[100]$ direction are given in Gauss

Table 2. The spin Hamiltonian parameters

*F P R, spectro- meter band	Temp.	g	$ b_4^0 $	$ b_6^0 $	$ B_4^0 $	$ B_4^4 $	$ B_6^0 $	$ B_6^4 $
Q	room	1.9921	18.52	0.57	0.3086	1.543	(4.5 ± 0.2)	(0.93 ± 0.02)
		± 0.0003	± 0.02	± 0.02	± 0.0002	± 0.002	$\times 10^{-4}$	$\times 10^{-2}$
X	room	1.9923	18.57	0.65	0.3095	1.548	(5.2 ± 0.2)	(1.1 ± 0.02)
		± 0.0002	± 0.02	± 0.02	± 0.0002	± 0.002	$\times 10^{-4}$	$\times 10^{-2}$

* Only the relative sign of b_4^0/b_6^0 is found and is negative. The parameters are given in $\times 10^{-4} \text{ cm}^{-1}$ units.

where $H_{\pm}$ are the magnetic field to the $|\pm M\rangle \rightarrow |\pm M \mp 1\rangle$ transitions.

The measured and calculated field values for the $\Delta M = \pm 1$ transitions are given in Table 1. The agreement is satisfactory using the first order perturbation theory. In Table 2 we list the calculated parameters of the spin Hamiltonian of equation (1) inferred from the values of Table 1 both for X and Q bands. The deviations at X band may be, in part, due to the neglect of second order perturbation.

An important inference from the gadolinium data is for the interpretation of the $4d$ and $5d$ group elements in the crystal field systems of A_2BX_6 . It is well known that these ions show a very large crystal field splitting leading towards a breaking of Hund's rule. It may be conjectured that this results in part from the nature of the $4d$ or $5d$ wavefunction and in part from the crystal field set up by the crystal hosts. The results of our data indicate that the crystal field compared with other octahedral complexes containing gadolinium is not very large and hence the main factor for the different magnetic behaviour must reside primarily in the $4d$ and $5d$ ions themselves.

Acknowledgement—We gratefully acknowledge assistance and criticism of Professor W. Low.

Microwave Division, S. S.
Department of Physics, A. G.
The Hebrew University,
Jerusalem.
Israel.

J. Phys. Chem. Solids, Vol. 31, pp 2581–2583

The magnetic susceptibilities of hexagonal Tc–Ru, Tc–Rh, and Ru–Rh Alloys*

(Received 6 February 1969, in revised form 5 March 1970)

BOOTH[1] has determined the magnetic susceptibility, χ , of a series of $4d$ transition metal alloys with the hexagonal closepacked

(hcp) structure, namely Mo–Ru, Mo–Rh, and Ru–Rh. Ho and Viswanathan[2] measured the electronic specific-heat coefficient, γ , of Mo–Ru and Mo–Rh alloys. From the results of magnetic susceptibility and electronic specific-heat measurements, Booth and Ho *et al.* concluded that to a large extent a rigid-band model provides a good description of these hcp alloys. We report the results of magnetic susceptibility measurements on Tc–Ru, Tc–Rh, and Ru–Rh alloys.

The alloys investigated were prepared from ruthenium and rhodium of 99.999 per cent purity. The elemental technetium was obtained from the Oak Ridge National Laboratory, and further purified by repeated arc melting to remove the volatile oxide impurities. One gram alloys were prepared by arc melting on a water-cooled copper hearth in a helium–argon atmosphere, and were homogenized at 1000°C. Since no weight loss was detected after preparation, the nominal composition of the alloys is assumed to be correct. X-ray and metallographic examinations confirmed that the alloys were homogeneous and had the hcp structure.

The magnetic susceptibility measurements

over the entire temperature and magnetic field range. Hence, only the χ values at 300°K are shown in Fig. 1 as a function of average group number (AGN). The AGN is numerically equal to the total number of s - and d -electrons per atom outside the krypton core. This, for technetium equals 7.0 and for ruthenium, equals 8.0. The susceptibility results for the technetium alloys show an AGN dependence similar to the molybdenum alloys[1], and the absolute values for Ru–Rh alloys are almost identical.

*This work was performed under the auspices of the United States Atomic Energy Commission.

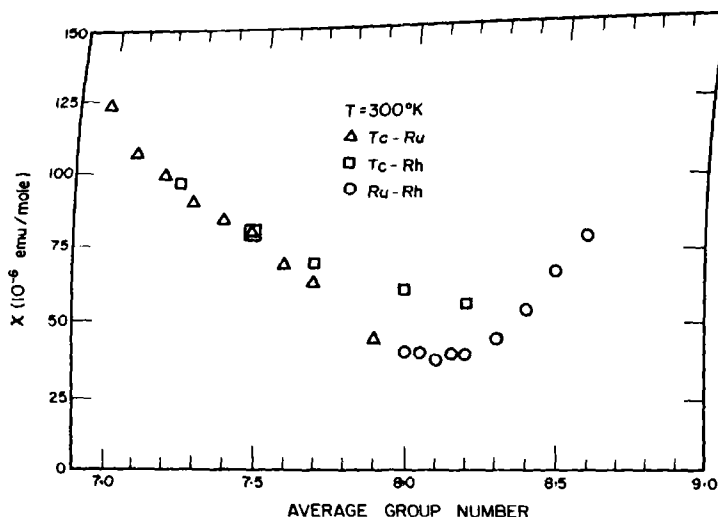


Fig. 1. Molar susceptibility at 300°K of Tc-Ru, Tc-Rh and Ru-Rh alloys as a function of average group number.

The measured susceptibility of transition metals and alloys is the sum of the contributions from (a) the diamagnetic susceptibility of the core and conduction electrons, (b) the orbital paramagnetism of the d -electrons [3], and (c) the spin susceptibility of s - and d -electrons, as expressed by the equation

$$\chi_{\text{meas}} = \chi_{\text{dia}} + \chi_{\text{orb}} + \frac{\chi_p}{1 - \phi N(E_F)}$$

where $\chi_p = 2\mu_B^2 N(E_F)$ is the Pauli spin susceptibility, ϕ is the electron-electron interaction, $N(E_F)$ is the density of states at the Fermi level for one direction of spin, and μ_B is the Bohr magneton. The diamagnetic contribution of the core electrons of technetium may be estimated from palladium data [4], and the value obtained is -27×10^{-6} emu/mole. The diamagnetic contribution of d -electrons may be neglected because of their high effective mass. The contribution of the s -electrons, calculated on the basis of the free-electron model, is about -2×10^{-6} emu/mole. Hence, the total diamagnetic contribution χ_{dia} for technetium is estimated as -30×10^{-6} emu/mole enhanced (E_F), value.

The orbital paramagnetism χ_{orb} of d -electrons is difficult to calculate, but for technetium an estimated value of 60×10^{-6} emu/mole was derived from Knight shift data [5]. When the estimated values for the diamagnetic susceptibility and orbital paramagnetism were combined with the measured value of 120×10^{-6} emu/mole.

To separate the enhanced spin-susceptibility into an enhancement factor, $1/(1 - \phi N(E_F))$, and spin susceptibility the density of states $N(E_F)$ must be known accurately. In the absence of an accurate $N(E_F)$ value an estimate of the order of magnitude of the enhancement factor may be made based on an $N(E_F)$ derived from the electronic specific heat coefficient γ . Using this method the assumption that electron-phonon interactions play only a minor role in the spin susceptibility enhancement must be noted. A measured γ value was not available for technetium, but a γ value for a Mo-Ru alloy of AGN equal to 7.0 was employed to estimate $N(E_F)$ and the spin-enhancement factor. An enhancement factor of 1.5 for the spin susceptibility was estimated in this manner.

Since the measured susceptibilities were

temperature independent, one may conjecture that the density-of-states curve is only slowly varying over the energy range represented by these alloys. Therefore, the spin-susceptibility enhancement factor was assumed nearly constant over the alloy composition range. By using the measured electronic specific-heat coefficient for ruthenium[2] and the estimated spin-enhancement factor for the alloy with AGN equal to 7, we calculate an enhanced spin susceptibility for ruthenium to be 60×10^{-6} emu/mole. When this value is combined with the measured susceptibility and the estimated diamagnetic susceptibility, the calculated value of χ_{orb} for ruthenium is 10×10^{-6} emu/mole.

In summary, the present magnetic susceptibility results for Ru-Rh alloys are in excellent agreement with the results reported[1]. Comparing the measured susceptibility values for Tc-Ru and Tc-Rh alloys with that of Mo-

Ru and Mo-Rh alloys reported by Booth[1], it is apparent that the magnetic susceptibility of hcp alloys of the second long period is only a function of AGN and is independent of the actual alloying species.

Acknowledgements—The authors wish to acknowledge the able technical assistance of Mr. J. Pasteris and Mr. R. Panosh.

Argonne National Laboratory,
Argonne,
Ill 60439,
U.S.A.

L. L. ISAACS
D. J. LAM

REFERENCES

1. BOOTH J. G., *Phil. Mag.*, **17**, 205 (1967).
2. HO J. and VISWANATHAN R., *J. Phys. Chem. Solids*, **30**, 169 (1969).
3. KURO R. and OBAI A. Y., *J. phys. Soc. Japan* **11**, 547 (1956).
4. LAM D. J. and MYLES K. M., *J. phys. Soc. Japan* **21**, 1503 (1966).
5. VAN OSTENBURG D. O., LAM D. J., SHIMIZU M. and KATSUKI A., *J. phys. Soc. Japan* **18**, 1749 (1973).

ERRATA

CARL WAGNER: Diffusion processes during the uptake of excess calcium by calcium fluoride. *J. Phys. Chem. Solids* **29**, 1925 (1968).

THE AUTHOR regrets that in Table 1 on page 1929:

- (i) The value of αn_{ex}^0 for $\ln a = 0.39$ is 179.5 instead of 175.9.
 - (ii) The value of $-(dy/d\lambda)_{x=0}$ for $\ln a = 0.35$ is 11.95 instead of 10.95 and that for $\ln a = 0.41$ is 52.27 instead of 50.27.
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M. V. RAO and W. A. TILLER: Excess free energies in the Ge, Si and Ga binary systems - The α -Parameter Approach. *J. Phys. Chem. Solids* **31**, 191 (1970).

THE AUTHOR regrets that in Fig. 7, page 198: $\Delta \bar{F}_{\text{ex}}^{\text{AS}}$ should read $\Delta \bar{F}_{\text{ex}}^{\text{AS}}$ in the coordinate and in the figure caption

A. IKUSHIMA: Anisotropy of temperature. *J. Phys. Chem. Solid*

THE AUTHOR regrets that on page 945 the numerical values should read, $c_{11} = 1.04$, $c_{12} = 0.86$, $c_{13} = 0.81$. On the same page in column 2 the sentence beginning on line one should read, "The angle θ takes an imaginary value while $\phi = 45.0^\circ$."

K. L. VANDER LUGT, J. COMAS and E. A. WOLICKI: Coloration of LiF produced by 3.0 MeV ^{40}Ar ions. *J. Phys. Chem. Solids* **30**, 2486 (1969).

THE AUTHORS regret that the calculation of the penetration depth of the 3.0 MeV ^{40}Ar ions into LiF is in error by 20 per cent. The value given was 1.64μ ; the

correct value is 2.053μ . This correction decreases the F -center concentrations given by 20 per cent, e.g. saturation of the F -center concentration occurs at 3.4×10^{19} F -centers/cc.

C. M. HURD and E. M. GORDON: The electronic structure of some copper and silver alloys with heterovalent solutes. *J. Phys. Chem. Solids* **29**, 2205 (1968).

THE AUTHORS regret that their derivation of equation (4.3) is incorrect. The problem arises from the assumed energy dependence of the residual resistivity, $\Delta\rho$. In its form (2.2) an energy-dependent term has already been evaluated through the substitution $k_r^3 = 3\pi^2 N/\Omega$, where the symbols have their usual meanings, and hence (2.2) is not suitable for the evaluation of Δx by direct substitution into equation (4.2). When all the energy-dependent terms are retained up to the differentiation in (4.2), the correct expression for Δx becomes

$$\Delta x = -E \left[-\frac{2}{E} + \frac{\sum_{l=1}^{l_{\max}} l \sin 2(\eta_{l-1} - \eta_l) \left(\frac{\partial \eta_{l-1}}{\partial E} - \frac{\partial \eta_l}{\partial E} \right)}{\sum_{l=1}^{l_{\max}} l \sin^2 (\eta_{l-1} - \eta_l)} \right]$$

(Note that in any case our (4.3) contained a misprinted exponent in the numerator, although our calculation had been carried out with the correct $\sin 2(\eta_{l-1} - \eta_l)$ factor as given above.)

Our calculated values of S_r/T given in Table 4 have to be modified in the following manner: for Cu-based alloys the absolute value of S_r/T in units of $10.9v/^\circ\text{K}^2$ is increased by 5.21, while that for Ag-based alloys is increased by 6.66. We emphasise that the phase-shifts and solute structures are unaffected by this correction, but the relatively good agreement between the experimental and calculated values of S_r/T is lost and the arguments of Section 4 are thereby considerably weakened.

Dr. Farrell of this group has asked us to point out that the same error was carried over into his calculations for some Ni alloys (*Phys. Rev.* **174**, 564 (1968)). However, in that work the consequences are less serious since less emphasis was placed upon quantitative comparison between the results of experiment and theory.

We are grateful to Dr. W. H. Young for pointing out this error to us and for useful correspondence.

R. K. CROUCH and T. E. GILMER, JR: Thermal ionization energy of lithium and lithium-oxygen complexes in single-crystal silicon. *J. Phys. Chem. Solids* **30**, 2037 (1969).

THE AUTHOR regrets that Dr. R. K. Franks, Appalachian State University, Boone, North Carolina, U.S.A., was omitted from the list of authors.

MÖSSBAUER SPECTROSCOPY OF ^{57}Fe AS A MAGNETIC IMPURITY IN HEUSLER ALLOYS

B. BJENSJO, B. SOLLY* and P. WIKFELDT

Chalmers University of Technology, Department of Physics, Gothenburg, Sweden

(Received 24 November 1969, in revised form 16 March 1970)

Abstract—Mössbauer absorption spectra have been obtained from ^{57}Fe as an impurity at the Mn sites in the Heusler alloys Cu_2MnAl and Cu_2MnSn as functions of temperature. The hyperfine field at $T = 0^\circ\text{K}$ is -200 and -196 kG for Cu_2MnAl and Cu_2MnSn , respectively. The isomer shift values at room temperature are -0.20 and -0.47 mm/sec relative to natural Fe and indicate a localization of conduction electrons to the Al and Sn atoms. The values of H_{eff} are consistent with the RKKY theory for spin-density oscillations.

1. INTRODUCTION

THE HEUSLER alloys have the form Cu_2MnX where $X = \text{Al, In, Sn, Ge}$ [1-3] and in the ordered state, are strongly ferromagnetic. The structure of these alloys, which was determined by Bradley and Rodgers [4] for the case of Cu_2MnAl , is shown in Fig. 1. The magnetic properties of these alloys are not properly understood and they have

Mössbauer atom has also been used to study hyperfine fields at the Sn nucleus in Cu_2MnSn [6, 7]. Furthermore, Caroli and Blandin [8] calculated the hyperfine fields at the Cu and Al atoms in Cu_2MnAl due to the Mn atoms using the model of virtual bound states suggested by Friedel and Anderson.

The aims of the present experiment were threefold:

(a) to ascertain whether such alloys can be

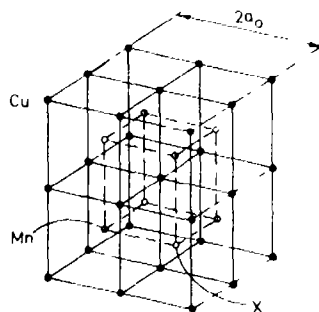


Fig. 1. Structure of Heusler alloys.

recently been restudied experimentally. Oxley *et al.* [3] have carried out measurements of magnetic properties and Sugibuchi and Endo [5] have measured the hyperfine fields at the Cu and Mn nuclei by means of NMR. The Mössbauer effect using ^{119}Sn as the

2. EXPERIMENTAL METHOD

A mixture of spec pure Cu and Mn and 10 per cent enriched ^{57}Fe was melted together in an alumina crucible in a high-frequency furnace and in an argon atmosphere. Al was then added to the ingot and the mixture was remelted and then quenched. The proportions were such as to give a nominal composition $\text{Cu}_{50}\text{Mn}_{23}\text{Al}_{23}\text{Fe}_2$. The resulting ingot was placed in a sealed silica tube in an atmosphere of extra-pure He, and homogenized 4 d at 770°C and quenched. The alloy was then

*Present address, AB Atomenergi, Nyköping, Sweden.

pulverised to a grain size suitable for both Mössbauer spectroscopy and X-ray powder diffraction (i.e. $\sim 25 \mu\text{m}$). This powder was annealed $\frac{1}{2}$ hr at 770°C in a He atmosphere to remove cold work and then quenched to room temperature. Part of the powder was sealed into a silica tube in a He atmosphere and aged 7 d at 200°C in order to increase the degree of ordering (3). X-ray powder diffraction was carried out on the alloy using a Guinier-Hägg focussing camera. The reflections were checked for position and intensity against the calculated values. The cellsize was also determined using a least-squares refinement computer program, as a check on the degree of stoichiometry. When it was clear that the alloy was of the desired type the composition was determined by means of chemical analysis. A similar preparation procedure was used for $\text{Cu}_2\text{MnSn}^{(57)\text{Fe}}$, the quenching and aging temperatures being 535 and 100°C respectively. Attempts to make $\text{Cu}_2\text{MnIn}^{(57)\text{Fe}}$ were unsuccessful, probably owing to the disturbing influence of Fe combined with the narrow range of stability for the Cu_2MnIn phase. Two large ingots of Cu_2MnAl , one undoped and one doped with natural Fe, were also prepared and heat treated in an identical manner to that described above. These alloys were then examined on a powder neutron diffractometer in an attempt to determine the positions of the Fe atoms in the Heusler alloy structure.

X-ray powder diffraction of the alloys gave patterns agreeing with the computed ones.

The alloys were shown to be single-phase with lattice parameters 5.948 , $6.153 \text{ \AA}$ for the Al and Sn alloys respectively. Subsequent chemical analysis gave the compositions $\text{Cu}_{49.4}\text{Mn}_{22.5}\text{Al}_{25.9}\text{Fe}_{2.2}$ and $\text{Cu}_{49.9}\text{Mn}_{23.9}\text{Sn}_{24.1}\text{Fe}_{2.1}$. Powder neutron diffraction of the doped and undoped Al alloys yielded different intensity relationships between the peaks for the doped and undoped alloys. This was to be expected since the nuclear scattering amplitudes of the elements involved differ widely. Table 1 shows the calculated and observed values of the total structure factor for the first 5 reflections, each normalized to that of the respective (220) reflection. From Table 1, the observed structure factors are, in general, lower for the doped material than for the undoped. The only case giving comparable changes in the calculated values is that when Fe goes to Mn sites. The quantitative agreement is not conclusive, however.

Specimens suitable for Mössbauer spectroscopy were prepared by pressing the powder between 2 discs of spectrographically pure Al foil in a metallographic press. The spectrometer was a conventional constant acceleration apparatus. The source was 15 mCi of ^{57}Co in a Pd matrix and was held at room temperatures for all runs. Low absorber temperatures were attained in a cryostat capable of reaching liquid He temperatures. For temperatures above room temperature a small heater-stage was constructed enabling the specimen to be heated in an inert atmosphere or static vacuum to temperatures

Table 1. Neutron diffraction intensities for doped and undoped Cu_2MnAl

hkl	Calculated $\frac{ F ^2}{ F_{220} ^2}$			Observed $\frac{ F ^2}{ F_{220} ^2}$		
	Undoped	Fe at Cu sites	Fe at Mn sites	Fe at Al sites	Undoped	Doped
111	0.35	0.34	0.28	0.34	0.65	0.29
200	1.11	1.07	0.86	0.99	1.22	0.74
220	1.00	1.00	1.00	1.00	1.00	1.00
311	0.24	0.23	0.16	0.24	0.26	0.28
222	0.95	0.93	0.72	0.83	1.70	0.68

$\sim 600^\circ\text{C}$. Lorentzian peaks were fitted to the measured spectra by a least-squares computer program and from the fitted curves the hyperfine field and isomer shift were calculated for the absorber at each temperature. Two final runs were made in which room temperature spectra were obtained in the absence of an external magnetic field and with a field of 12.6 kG applied to the absorber in order to determine the sign of the hyperfine field.

3. RESULTS

The Mössbauer spectra at low temperatures had six peaks which, as the temperature increased, moved together and finally coalesced at the Curie point. (See Fig. 2 for representative spectra.) The low temperature aging made the Mössbauer spectra considerably more distinct. The fitted curves were analysed and the hyperfine field was calculated as a function of temperature. The hyperfine field showed a variation with temperature

similar to the variation of the magnetization for temperatures between liquid nitrogen temperature and room temperature. These values are plotted in Fig. 3. The hyperfine field for Cu_2MnSn was not measured at elevated temperatures owing to the occurrence of a phase transformation at a temperature below the Curie point (3). If a $T^{3/2}$ extrapolation is carried out for the hyperfine field values for Cu_2MnAl , a value of the Curie point of 520°K (cf. 630°K in (3)) is obtained (marked T_c in Fig. 3). Values of the isomer shift relative to natural Fe at room temperature and hyperfine field are given in Table 2. The application of an external magnetic field to the absorber caused a distinct decrease in the hyperfine splitting indicating a negative field at the Fe nucleus.

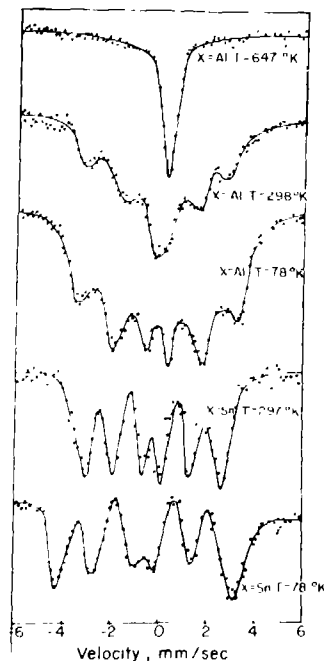
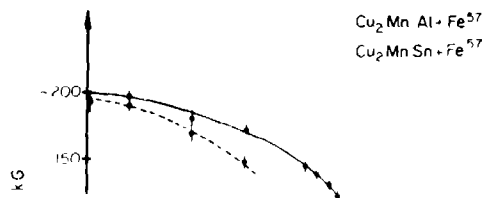


Fig. 2. Representative Mössbauer spectra for $\text{Cu}_2\text{MnAl} + ^{57}\text{Fe}$.



4. DISCUSSION

Since a single six-line spectrum was obtained at low temperatures we can reasonably assume that the Fe replaces only one atomic species in the alloy, most probably the Mn. Also, if Fe goes to the Mn sites then an Fe atom will lie in an environment free from other Fe atoms out to the 3rd nearest neighbour. Thus we can neglect Fe-Fe interactions and the Fe nucleus will lie in an environment due to the parent atom and a Heusler alloy matrix.

Table 2. Mössbauer data as a function of temperature

T(°K)	Cu ₂ MnAl + ⁵⁷ Fe		Cu ₂ MnSn + ⁵⁷ Fe	
	H _{eff} (kG)	Isomer shift (mm/sec)	H _{eff} (kG)	Isomer shift (mm/sec)
4	—	—	-196	—
78	-196	—	-194	—
195	180	—	172	—
298	168	-0.20	149	-0.47
411	143	—	—	—
431	-138	—	—	—
453	130	—	—	—
471	-120	—	—	—
490	107	—	—	—
519	5	—	—	—
554	0	—	—	—
594	0	—	—	—

Isomer shift

The experimental values of the isomer shift at room temperature relative to natural Fe are -0.20 and -0.47 mm/sec for Cu₂MnAl and Cu₂MnSn respectively. We believe that the 3*d* electrons of the Mn and Fe atoms in these alloys are to be described by overlapping spin split resonant bound states which will result in there being approximately 6 and 7 *d* electrons in Mn and Fe respectively. Furthermore we shall assume that the number of 3*d* electrons per atom of Fe dissolved in Cu₂MnX is not significantly different from that for an atom in pure iron metal.

Experimentally we find

$$\rho_{Fe}(0) \approx \rho_{Al}(0) \approx \rho_{Sn}(0)$$

where $\rho_{Fe}(0)$ is the electron charge density at an Fe nucleus in natural Fe and $\rho_i(0)$ is the corresponding quantity for Fe dissolved in Cu₂MnX. This sequence we believe is due to the different valencies. Cu and Mn have valency 1 in these alloys and the extra charge associated with the trivalent Al and quadrivalent Sn atoms must be localised to these atoms to provide adequate screening of the ions and to maintain electrostatic neutrality. As is known there are oscillations in the screening charge density and thus there can be significant density of this screening

charge at neighbouring atoms; the isomer shifts imply that this latter quantity is greater in the Sn than in the Al alloy in keeping with the larger valence.

Hyperfine field

The total hyperfine field at the Fe nucleus is the sum of four components[9, 10]. In ferromagnets with cubic symmetry, the only important components are the orbital contribution, H_L , and the Fermi contact term, H_F . In Cu₂MnAl $g = 1.993$ for Mn (11), and hence the crystal field is such that the orbital moment is almost completely quenched and H_L is therefore negligible in these alloys.

Thus the only contribution of importance in the case of the Heusler alloys is H_F , the Fermi contact term. This term can be conveniently separated into two parts: $H_F = H_c + H_e$ where H_c and H_e are the fields due to exchange polarization of the core *s*-shells and the outer 4*s* conduction electrons, respectively. H_c is given by $H_c = -S\chi_c$ where S is the Bohr magneton number and χ_c is a measure of the spin polarization. χ_c has been calculated for the 3*d* transition metals in atomic and ionised states by Watson and Freeman[12]. They found that $\chi_c(\text{Mn}) = \chi_c(\text{Fe})$ and also that χ_c is sensitive to the spatial distribution of the 3*d*-electrons. Both the Heusler alloys and natural Fe have a bcc structure and approximately the same lattice parameter. We shall therefore assume χ_c to be the same for Fe and Mn atoms in Heusler alloys and for Fe in natural Fe, H_c being decided only by the magnetic moment of the Fe or Mn respectively. This means that H_c for Mn in Cu₂MnX is numerically larger (i.e. more negative) than H_c for Fe in natural Fe.

$H_e \propto \rho_i(0) \cdot p$ where $\rho_i(0)$ and p are the conduction electron charge density and spin polarization at the nucleus, respectively[10]. In natural Fe, H_e is most probably negative [13, 14] and relatively small. According to the RKKY theory, spin-polarization of the conduction electrons can be described by the

function $[\sin(2k_F r) - 2k_F r \cos(2k_F r)]/(2k_F r)^4$ where r is the distance from the magnetic impurity atom and k_F is the wave vector at the Fermi surface. This function has nodes at $2k_F r = 4.5, 7.7, 11.0, 14.1$ as is shown schematically in Fig. 4. In natural Fe, the

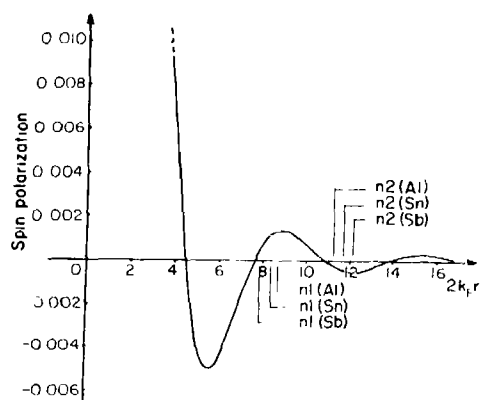


Fig. 4 Spin-polarization of conduction electrons vs. $2k_F r$ showing the positions of the Mn neighbours, e.g. $n2(\text{Sn})$ is the position of the 2nd Mn neighbour in Cu_2MnSn .

nearest and n.n. neighbours give rise to a negative polarization at a particular atom [15]. Experimentally the sum of the contributions of successive coordination shells is measured, and for Fe, this sum is negative. In Cu_2MnX , however, the nearest and n.n. neighbours of a Mn atom are Cu and X respectively, since neutron diffraction measurements show that there is no spin polarization associated with the Cu and X atoms [16] they do not contribute to the polarization at the Fe or Mn nuclei. We therefore expect that H_i is positive in Cu_2MnX and that its magnitude can be relatively large compared with H_i in Fe, thus, despite the fact that the magnetic moment of Fe in Cu_2MnX is probably larger than in natural Fe, it is reasonable that H_{eff} for Fe in Cu_2MnX is smaller in magnitude than in natural Fe.

The magnetic moment of Mn in Cu_2MnAl has been measured by Oxley to be $4.1 \mu_B$ [3]. Moreover, the magnetic moment of Mn in

Cu_2MnIn has been found to be $4.0 \mu_B$ [2, 3]. More recent measurements [17] have yielded a value of $3.6 \mu_B$ for natural Cu_2MnAl . The latter value agrees more closely with H_{eff} for Mn in Cu_2MnAl and Cu_2MnIn as measured by NMR [5] assuming proportionality between H_{eff} and magnetic moment. (There are, in fact, cases where the hyperfine field at the impurity atom does not follow the host magnetization, but the rule seems to apply in the majority of cases.) The magnetic moment of Fe in Cu_2MnAl is unlikely to be greater than $3 \mu_B$. The values of $3 \mu_B$ and $3.6 \mu_B$ agree relatively well with H_{eff} as measured at Fe and Mn in Cu_2MnAl [5].

We have $H_i \propto \rho_i(0)p$. Isomer shift measurements yield $\rho_i(0)$ for Fe in Cu_2MnSn to be greater than $\rho_i(0)$ for Cu_2MnAl . If p is the same for both alloys, then H_i should be greater for Cu_2MnSn than Cu_2MnAl . This is not the case since H_{eff} is approximately the same in both alloys. However, $\rho(\text{Cu}_2\text{MnAl}) < \rho(\text{Cu}_2\text{MnSn})$ is in agreement with the RKKY theory. Using a free-electron model for calculation of k_F , the nearest Mn neighbour to Fe is at $2k_F r = 7.9, 8.4, 8.7$ and

case, is still ferromagnetic, but the small negative contribution of the n.n. Mn neighbours results in a value of I_i less than that of Cu_2MnAl [8]. This decrease in p for Cu_2MnSn compared with Cu_2MnAl results in H_i being approximately the same in the two alloys.

5. CONCLUSIONS

These alloys can be doped with ^{57}Fe as a Mossbauer probe and the Fe appears to replace a single atomic species, namely Mn. Isomer shift measurements are consistent

with a localization of conduction electrons to the X-atom.

The measured values of H_{eff} at an Fe impurity in these two alloys and the relationship between these values is consistent with the RKKY theory for spin-density oscillations. Any interpretation of such experiments must, however, at present, be tentative and qualitative owing to the impossibility of separating the conduction electron and core polarization contributions to H_{eff} .

Acknowledgements — The authors wish to thank Professor H. P. Myers for suggesting this investigation and for valuable discussions during its development. One of us, P. W., also wishes to acknowledge the award of a research grant from AB Atomenergi, Nyköping.

REFERENCES

1. HEUSLERO, *Ann. Phys.* **19**, 155 (1934).
2. COLES B. R., HUME-ROTHERY W. and MYERS H. P., *Proc. R. Soc. A* **196**, 125 (1949).
3. OXLEY D. P., TEBBIE R. S. and WILLIAMS K. C., *J. appl. Phys.* **34**, 1362 (1963).
4. BRADLEY A. J. and RODGERS J. W., *Proc. R. Soc. A* **144**, 340 (1934).
5. SUGIBUCHI K. and ENDO K., *J. Phys. Chem. Solids* **25**, 1217 (1964).
6. CHEKIN V. V., DANILENKO L. E. and KAPLIENKO A. I., *Soviet Phys.-JETP* **24**, 472 (1967).
7. KUZMIN R. N., IBRAIMOV N. S. and ZHDANOV G. S., *Soviet Phys.-JETP* **23**, 219 (1966).
8. CAROLI B. and BLANDIN A., *J. Phys. Chem. Solids* **27**, 503 (1966).
9. MARSHALL W. and JOHNSON C. F., *Metallic Solid Solutions* 29 (edited by J. Friedel and A. Guimer) Vol. 29, p. 1 (1969).
10. MARSHALL W., *Phys. Rev.* **110**, 1280 (1958).
11. SCOTT G. G., *Phys. Rev.* **121**, 104 (1961).
12. WATSON R. E. and FREEMAN A. J., *Phys. Rev.* **123**, 2027 (1961).
13. RADO G. T. and SUH H., *Magnetism* **2A**, 167 (1965).
14. ANDERSON D. H., *Solid State Commun.* **4**, 189 (1966).
15. STEARNS M. B., *Phys. Rev.* **147**, 439 (1966).
16. FELCHER G. P., CABLE J. W. and WILKINSON M. K., *J. Phys. Chem. Solids* **24**, 1663 (1963).
17. ENDO K., OHYAMA T. and KIMURA R., *J. phys. Soc. Japan* **19**, 1494 (1964).

HOT EXCITONS AND EXCITON EXCITATION SPECTRA

E. GROSS, S. PERMOGOROV, V. TRAVNIKOV and A. SELKIN

Institute of Semiconductors, Academy of Sciences of the USSR, Leningrad U.S.S.R.

(Received 7 November 1969, in revised form 9 March 1970)

Abstract—Excitation Spectra (E.S.) of free exciton emission in CdS crystals are measured at 4-2 and 77°K both for zero-phonon emission lines ($n = 1A$, $n = 1B$ and $n = 2A$) and for line of exciton annihilation with simultaneous creation of LO phonon ($A_1 - LO$). Distinctly pronounced oscillating structure with energy period of LO phonon can be observed in the E.S. of all exciton emission lines. This structure arises due to kinetic energy relaxation processes in exciton bands, the appearance of oscillations is conditioned by incomplete thermalization of excitons during exciton life-time. Observation of discrete structure in the E.S. permits one to draw some conclusions concerning the mechanism of exciton formation under optical excitation. Creation of excitons with kinetic energies up to 0.2 eV, considerably exceeding the binding energy 0.03 eV, was observed. Non-equilibrium character of zero-phonon free exciton emission is briefly discussed.

1. INTRODUCTION

SINCE the discovery of exciton optical spectra in Cu_2O crystals 17 yr ago [1], a large number of theoretical and experimental investigations on the exciton spectra in semiconductor crystals [2] have been carried out. Energy level positions of a free exciton, the selection rules and oscillator strengths of optical transitions into exciton states, the symmetry properties of exciton states and the influence of the external fields (electric, magnetic, uniaxial stress) on exciton levels were investigated extensively. Thus the considerable information about the exciton band structure near the Brillouin zone center $K = 0$ was gained.

However, up to the present time rather poor information exists about the exciton kinetic properties such as: formation under optical excitation, relaxation to the thermal equilibrium state and diffusion in crystals. These properties are of considerable interest since excitons play a significant role in the processes of energy transfer and, to a great extent, determine such phenomena as photoconductivity and light emission in solids. Besides, the knowledge of exciton kinetics is very important in order to predict the possibility of

observing new properties of exciton gas such as Bose--condensation [3, 4] and metallization [5]. These phenomena are expected at high exciton concentrations in crystals cooled to very low temperatures.

Some information on the free exciton kinetic

properties is obtained by studying the dependence of the E.S. on the excitation intensity, corresponding to the strong absorption lines on the edge of fundamental absorption. Both the minima and maxima in E.S. can appear at the frequencies of absorption lines [11], the general appearance of the spectra depending on the interrelation between the absorption coefficient, the diffusion length and the rate of surface recombination of photo-excited free carriers or excitons [12, 13].

In some cases the E.S. of photoconductivity and emission also show the regular oscillating structure which is connected with the

kinetics of energy relaxation of elementary excitations and does not reflect the structure in the absorption spectrum. Such oscillations in photoconductivity E.S. in InSb were first reported by Stocker *et al.*[14] and in InSb and GaSb by Habegger and Fan[15]. Later similar oscillations were also found in the photoconductivity E.S. of CdS and CdSe [16, 17], ZnTe[18], GaP[19], diamond [20], Ge and CuCl[21]. Oscillating structure in the E.S. of impurity emission was observed in diamond[22], GaP[23], ZnSe[24] and CdS [24–26]. In most of these cases the oscillating progression of maxima or minima was connected with the ground state exciton level.

However, both photoconductivity and impurity emission arise as a result of interaction of free excitons with impurities. So the information about free exciton kinetics can be deduced from both types of E.S. only on the ground of the supplementary presumptions about the dependence of mobility or capture cross-section on kinetic energy.

Most convenient for the study of free exciton kinetics are the E.S. of *free exciton* emission. Due to the conservation of energy and momentum in the processes of radiative exciton annihilation every point in the free exciton emission spectrum is connected with a certain point of exciton band[7]. The study of E.S. of this emission can provide direct information about the exciton kinetics in different points of exciton band.

In the present work we have measured the E.S. of free exciton emission in CdS crystals at 4·2 and 77°K. For different exciton states ($n = 1A$, $n = 2A$ and $n = 1B$) strongly pronounced oscillations in the E.S. were found, the separation between maxima being equal to the energy of an I.O phonon and the position of series depending on the exciton state under investigation. The appearance of these oscillations is conditioned by incomplete thermalization of excitons during their life-time.

As it follows from our experiments, 'hot' excitons, i.e. excitons, the kinetic energy of

which considerably exceeds the mean thermal value,—can be detected in the E.S. of free exciton emission.

2. EXPERIMENTAL

Excitation Spectr: (E.S.) of exciton emission in CdS crystals were obtained with an optical system consisting of two prism monochromators. The crystal, directly immersed in liquid helium or nitrogen, was excited by a monochromatic light-beam, which was selected with the first monochromator ('source') from a continuous spectrum of an incandescent lamp. The second monochromator ('receiver') was used for dispersion of the crystal emission. By selecting different lines in the free exciton emission spectrum and scanning the wavelength of exciting light, we determined how the intensity of the exciton emission line in question depended on the frequency of exciting light. It is this dependence which is called the Excitation Spectrum (E.S.).

All the E.S. presented in our paper are original recordings without corrections on the spectral distribution of exciting intensity. Such corrections, as our investigation shows, do not significantly alter the general appearance of the obtained E.S.

The investigated CdS single crystals were thin (100–200 μ) platelets grown from the vapour phase. Samples with sufficiently intense resonant free exciton emission lines at 77°K were selected. These crystals, as a rule, had a rather weak 'edge emission' in the green region and a low intensity of lines, which appeared due to radiative annihilation of free excitons with simultaneous creation of I.O phonons. In all, more than 30 samples were investigated. Emission intensity and shape of peaks in the E.S. slightly differ in various samples. However, the positions of peaks and general character of the E.S. are the same for all investigated samples.

3. EXPERIMENTAL RESULTS

The emission spectrum of free excitons in

CdS crystal contains both lines caused by the zero-phonon annihilation of free excitons and lines arising from annihilation of excitons with a simultaneous creation of LO phonons in the lattice. As a result of the momentum conservation in the emission process, zero-phonon lines appear at annihilation of excitons with the wavevector and kinetic energy almost exactly equal to zero (the bottom of exciton band). In LO phonon assisted processes excitons with any wave-vectors may take part. The shape of exciton-phonon emission lines reflects the exciton kinetic energy distribution in the exciton band.¹

At $T = 4.2^\circ\text{K}$ lines of zero-phonon exciton annihilation $n = 1A$ ($\lambda = 4853 \text{ \AA}$), $n = 1B$ ($\lambda = 4825 \text{ \AA}$) and $n = 2A$ ($\lambda = 4814 \text{ \AA}$) approximately coinciding with the corresponding lines in the absorption spectrum [27, 28] can be detected in the emission spectrum of CdS crystals (Fig. 1). Besides, lines of $n = 1A$ exciton annihilation with a simultaneous creation of one ($A - 1LO$, $\lambda = 4928 \text{ \AA}$) and two ($A - 2LO$, $\lambda = 5007 \text{ \AA}$) LO-phonons are observed in the emission spectrum [7]. In our samples these lines (not shown in

Fig. 1) are weak and lie upon a rather strong background of continuous emission. At $T = 4.2^\circ\text{K}$ very intense emission lines of bound excitons are also present in the spectral region of $4860\text{--}4890 \text{ \AA}$ [29].

The emission spectrum of CdS crystals at $T = 77^\circ\text{K}$ is shown in Fig. 2. It contains zero-phonon lines $n = 1A$ ($\lambda = 4870 \text{ \AA}$) and $n = 1B$ ($\lambda = 4840 \text{ \AA}$) and phonon-assisted exciton annihilation lines ($A - 1LO$) and ($A - 2LO$).

We have recorded the E.S. of resonant emission lines $n = 1A$ and $n = 1B$ at $T = 4.2^\circ\text{K}$ and 77°K , and line $n = 2A$ at $T = 4.2^\circ\text{K}$. The characteristic general feature of obtained spectra is the existence of an oscillating structure of sharp maxima, separated in the spectra by the energy of an LO-phonon (0.0383 eV)². The energy position of the very first long-wave maximum in every E.S. exceeds the energy of the exciton emission line under investigation also by the energy of LO phonon. In Fig. 3 and 4 E.S. of zero-phonon exciton emission lines at $T = 4.2^\circ\text{K}$ and 77°K are given. The maxima positions in the $I(\lambda)$ vs. λ plots correspond to the positions between

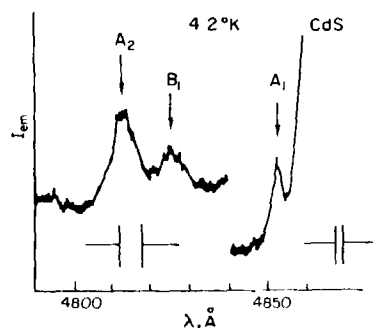


Fig. 1. Emission spectrum of CdS single crystals at $T = 4.2^\circ\text{K}$ in the region of zero-phonon free exciton lines. Resonant emission lines $n = 1A$ (A_1), $n = 1B$ (B_1) and $n = 2A$ (A_2) are marked by arrows. Gain in the left part of spectrum is increased by the widening of spectral slit width.

¹The shape of free exciton emission lines and the principal regularities carried out in the processes of exciton radiative annihilation, are discussed in detail in our previous paper [7].

or: maxima width increases and then intensity drops. In samples with bright exciton emission it is possible to observe up to 7 distinct maxima in the E.S. of zero-phonon $n = 1A$ line. Besides the oscillating structure, a certain continuous background, also dropping to the short-wave side, is observed in the E.S. of $n = 1A$ line.

In some cases the minima or maxima on the positions of the strong absorption lines are also present in the E.S. of free exciton emission. This phenomenon is evidently analogous to the behaviour of exciton absorption lines in photoconductivity [13] and is not discussed here.

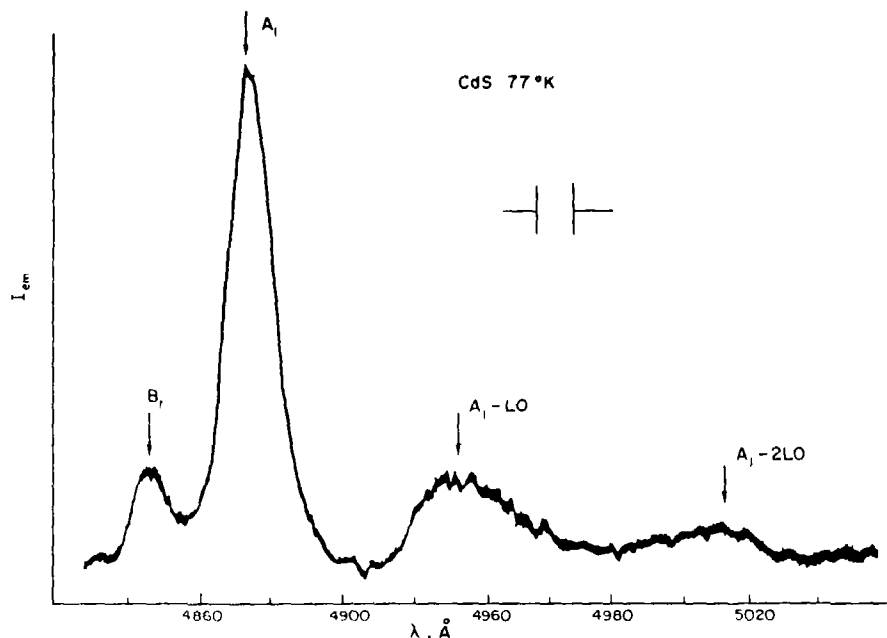


Fig. 2. Free exciton emission spectrum of CdS single crystals at $T \approx 77^\circ\text{K}$. Besides resonant emission lines $n = 1A$ (A_1) and $n = 1B$ (B_1), $n = 1A$ exciton annihilation lines with simultaneous creation of one ($A_1 - 1O$) and two ($A_1 - 2LO$) longitudinal optical phonons can be observed in the spectrum.

The study of the maxima shapes in the E.S. of other zero-phonon exciton emission lines is impeded due to the poor resolution in these weak spectra. However, as seen in Fig. 3 and 4, the E.S. of all zero-phonon lines have a similar character and do not suffer any drastic change on rising the temperature from 4.2 to 77°K .

At $T = 77^\circ\text{K}$ in the E.S. of the $A - 1O$ line an oscillating structure with a LO phonon energy period is also clearly seen (Fig. 4). In this case the maxima positions of the equidistant series in the E.S. depend on the wave-length, selected by the receiving monochromator.

Different points of the $A - 1O$ line correspond to annihilation of excitons with a different kinetic energy [7]. Since the spectral slit width of the receiving monochromator in our experiments was considerably less than the width of the $A - 1O$ line, we could separately record

the emission of excitons with different kinetic energies.

In Fig. 5 the position of the first two maxima in the E.S. of the $A - 1O$ line is given as a function of the kinetic energy of $n = 1A$ annihilating exciton. The latter can be evaluated as an energy difference between the position of the receiving monochromator in the $A - 1O$ spectrum and the point, shifted to the lower energy side of the zero-phonon emission line by the energy of LO phonon [7]. As seen from the Fig. 6, the maxima in the E.S. are always shifted by the integer number of LO phonons in relation to the energy of exciton under observation.

The same regularities were observed in the E.S. of $A - 2LO$ emission line at 77°K .

We also studied the E.S. of bound exciton emission lines in CdS crystals at 4.2°K . Like the authors of [24] and [26], in this case we have also found an oscillating struc-

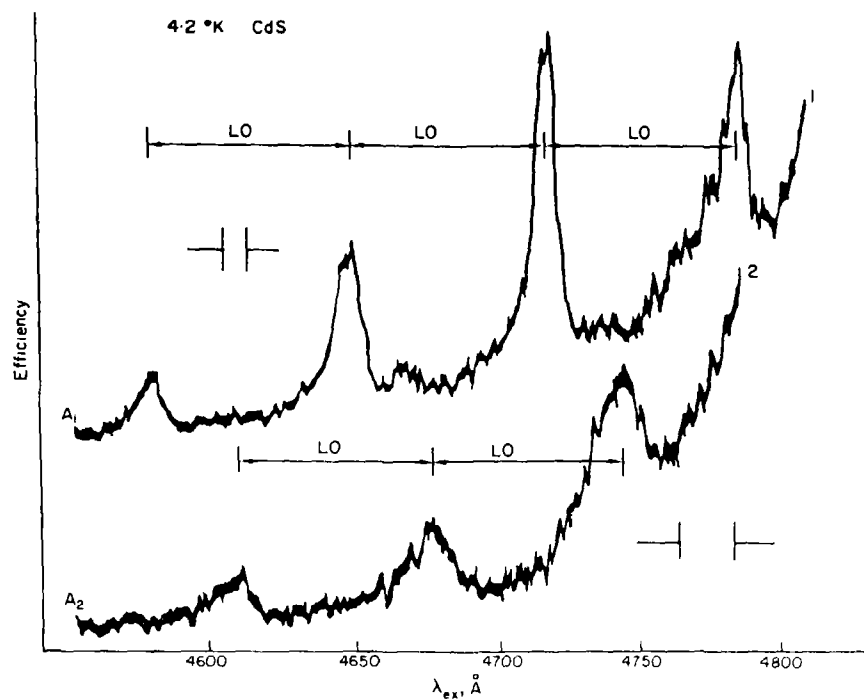


Fig. 3. Excitation spectra (F S) of free exciton emission resonant lines $n = 1A$ (A_1) and $n = 2A$ (A_2) in CdS crystals at 4.2 °K.

Table 1. Positions of maxima separations between maxima ΔE emission lines $n = 1A, 2$

Emission line (Å, eV)	Maxima				
	+LO	+2LO	+3LO	+4LO	+5LO
$n = 1A$					
$\lambda = 4854$	4782	4712	4646	4583	4519
$E = 2.554$	2.592	2.631	2.668	2.705	2.743
ΔE (eV)	0.038	0.039	0.037	0.037	0.038
$n = 1B$					
$\lambda = 4826$	4755	4688	4621	4552	
$E = 2.569$	2.607	2.644	2.683	2.723	
ΔE (eV)	0.038	0.037	0.039	0.040	
$n = 2A$					
$\lambda = 4814$	4742	4674	4609	4546	
$E = 2.575$	2.614	2.652	2.690	2.726	
ΔE (eV)	0.039	0.038	0.038	0.036	

Table 2. Positions of maxima in excitation spectrum (E.S.) and separations between maxima ΔE in E.S. of free exciton resonant emission lines $n = 1A$, $n = 1B$ at 77°K

Emission line (λ , eV)	Maxima positions in E.S. (λ , eV)					
$n = 1A$	+ 1LO	+ 2LO	+ 3LO	+ 4LO	+ 5LO	+ 6LO
$\lambda = 4871$	4798	4730	4660	4596	4532	4471
$E = 2.545$	2.583	2.621	2.660	2.697	2.735	2.773
ΔE (eV)	0.038	0.038	0.039	0.037	0.038	0.038
$n = 1B$	+ 1LO	+ 2LO	+ 3LO	+ 4LO	+ 5LO	
$\lambda = 4845$	4773	4699	4633	4570	4504	
$E = 2.559$	2.597	2.638	2.676	2.712	2.750	
ΔE (eV)	0.038	0.039	0.038	0.036	0.038	

ture in E.S. of some emission lines. However, the E.S. are more complicated for bound excitons than for free excitons, and the maxima in these spectra have a fine structure. This fine structure, and the conditions of its observation will be described in our following paper.

4. DISCUSSION

The study of free exciton emission E.S. in CdS crystals shows that the efficiency of this emission considerably drops as the exciting photon energy increases. The most effective excitation of the excitons with the given energy takes place when the energy

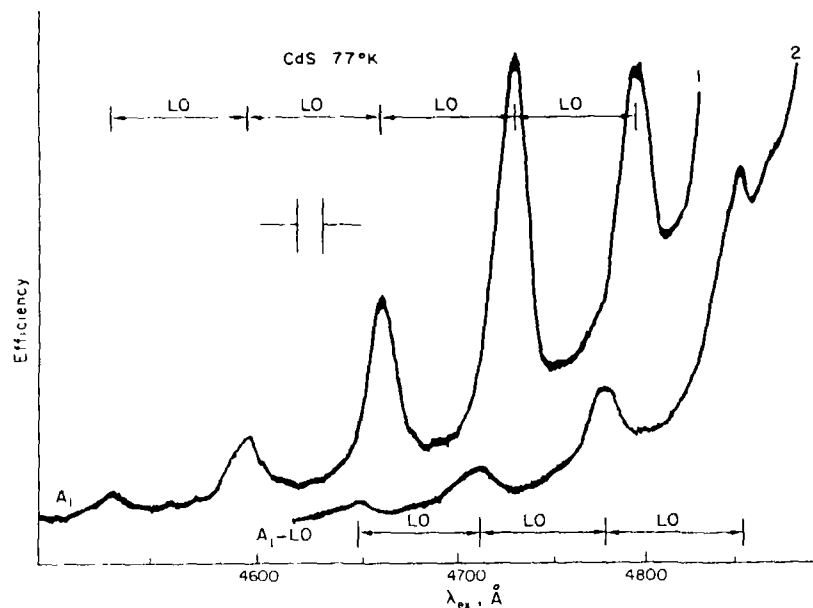


Fig. 4. Excitation spectra (E.S.) of exciton emission in CdS crystals at 77°K for $n = 1A$ (A_1) resonant line and for the part of phonon assisted exciton annihilation line ($A_1 - 1LO$) (See text)

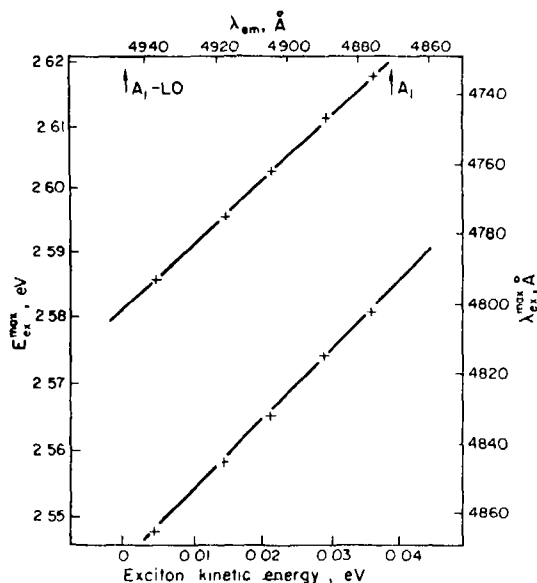


Fig. 5. Dependence of two first maxima positions (λ_{ex}^{max} , E_{ex}^{max}) in the F.S. of the single phonon assisted exciton annihilation (A_1-LO) on kinetic energy (E_{kin}) of observed exciton in the (A_1-LO) spectrum at 77°K. Experimental results are represented by crosses, abscissa being the position of receiving monochromator in the emission spectrum, the ordinate—position of maximum in F.S. Kinetic energy of annihilating exciton E_{kin} may be calculated in the emission spectrum as the difference between the detected energy and the energy displaced below $n = 1A$ resonant line by the energy of one LO phonon.

of the exciting photons exceeds the energy of the exciton under observation by integer number of LO-phonons. Such regularity has been experimentally established both for excitons with a zero kinetic energy (for resonant emission lines $n = 1A$, $n = 1B$ and $n = 2A$) and for excitons at a general point of the exciton band (in the E.S. of $A-LO$ line).

The positions of the maxima in the F.S. of free exciton emission differ for different exciton lines and do not coincide with the positions of absorption lines in the region of fundamental absorption[30]. Therefore it is natural to connect the structure in the E.S. with the kinetic phenomena in the exciton bands.

In order to explain the observed phenomena, it is most plausible to assume that the thermal quasiequilibrium is not completely established in the exciton band within the time preceeding the radiative annihilation of free excitons.*

As can be seen from the comparison of the E.S. of different lines in the free exciton emission spectrum, the intensity distribution in this spectrum depends on the frequency of the exciting light. Such a dependence is characteristic of non-equilibrium emission processes[32].

It may be assumed that excitons, created with a high kinetic energy, excite LO phonons in crystal and very quickly lose excess of kinetic energy equal to an integer number of LO-phonons. But equilibrium of exciton kinetic energies with the lattice temperature can only occur as a result of excitation and absorption of a large number of acoustical phonons. This process is far slower than the interaction with LO phonons, and is not completed during the exciton life-time†

Figure 6 shows how an incomplete establishment of thermal equilibrium in exciton

phonons above point E' , the successive relaxation process with the emission of LO phonons only will lead them to point E' . High population rate of E' in this case will result in a high emission intensity of E' excitons, and the maximum in the E.S. will be observed.

*A similar assumption was made by Goto and Ueta [31] for explanation of the oscillating structure in F.S. of exciton emission in CuBr crystals.

†We assume that the probability of exciton interaction with LO phonons is much higher than with acoustical ones. Theoretical works[33, 34] justify this assumption for ionic semiconductor crystals.

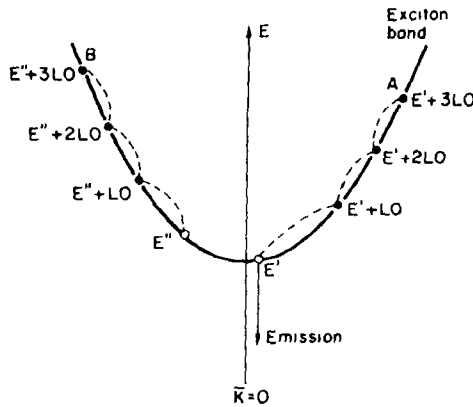


Fig. 6 Schematic representation of successive (A) and incompletely successive (B) LO phonon relaxation processes in exciton population of point E'

Excitons, created at point B (Fig. 6), can reach E' point only after the emission of a large number of acoustical phonons. Therefore, a great probability exists that an exciton will not reach point E' during its life-time. The excitation efficiency of exciton emission from point E' will in this case be low (minimum in the E.S.).

Let us now consider the process of exciton formation under optical excitation.

There are two possible ways of exciton formation at light absorption in the fundamental region. Firstly, excitons can be formed from free electron-hole pairs, generated in the process of interband absorption. Besides, the exciton formation is possible by indirect exciton absorption. As a result of it an exciton and phonon appear in the crystal. The study of indirect exciton optical transitions in CdS crystals [7, 35] shows that such transitions most probably occur with LO phonon participation.

For the observation of oscillating structure in the E.S. of free excitons, in the case of exciton formation from free carriers, it is necessary that electrons and holes do not thermalize by interaction with acoustical phonons before the binding. In such a case the binding should take place for particles

with a rather high relative speed. The probability of this process is low. A much higher binding probability exists for completely thermalized carriers with low relative speed.* However, no oscillating structure should be observed in the E.S. in this case.

In order to explain our experimental data we assumed that the exciton formation in the region of oscillating structure of E.S. is a result of indirect exciton absorption. The energy conservation law for simultaneous optical creation of exciton and one LO phonon in a crystal is:

$$h\nu = E_0 + E_{\text{kin}} + h\omega_0 \quad (1)$$

where $h\nu$ is the energy of absorbed photon, E_0 — the energy at the bottom of the exciton band, E_{kin} — kinetic energy of created exciton, $h\omega_0$ — energy of LO phonon, which conserves momentum in absorption process.

As it follows from (1), an indirect exciton absorption begins at photon energy $h\nu = E_0 + h\omega_0$ and passes continuously into the high energy region as the kinetic energy of created excitons increases. In the region of small exciton kinetic energies, the absorption coefficient for this process is proportional to $E_{\text{kin}}^{3/2}$ [34, 35]. At high energies this absorption coefficient should drop due to a decrease of the exciton-phonon interaction probability at large wave-vectors K [33].

Thus, creation of excitons due to indirect optical transitions is possible in a wide region of the fundamental absorption, the kinetic energy of created excitons determined by:

$$E_{\text{kin}} = h\nu - E_0 - h\omega_0. \quad (2)$$

If only LO phonon relaxation is completed during the exciton life-time, the formation of excitons with some definite kinetic energy E' will take place at photon energies

$$h\nu = h\nu_0 + nh\omega_0 \quad (3)$$

*Binding of carriers into the exciton was discussed by Lipnick [36].

where n is an integer, and $h\nu_0$ —minimum photon energy, leading to the formation of excitons with E' .

In this case a series of very narrow maxima at photon energies, determined by equation (3) must appear in the E.S. of exciton emission. Emission and/or absorption of acoustical phonons in the process of kinetic energy relaxation will broaden these maxima. Since at low temperatures phonon emission is more probable than absorption, the maxima in the E.S. should be asymmetric with the short-wave side wider, than the long-wave one.

Investigation of indirect exciton emission spectra in CdS crystals [7] showed, that in the region of small wave vectors indirect optical transitions with simultaneous creation of two LO phonons may have the probability comparable with that of an one-phonon process. This process will cause continuous absorption beginning at photon energy

$$h\nu = E_0 + 2h\omega_0 \quad (4)$$

and passing into the high energy region with the increase of exciton kinetic energy. In the high energy region this absorption, like a single-phonon one, should also decrease. The process of oscillation formation in the E.S. due to two phonon indirect absorption does not differ essentially from the case of single-phonon absorption.

Indirect optical transitions with simultaneous creation of 3 or more LO phonons should have small probability in CdS crystals. Such transitions were not observed in the indirect exciton emission spectrum in CdS crystals [7].

In order to learn the mechanism of exciton formation in CdS crystals at optical excitation, we have studied the dependence of exciton emission intensity on the intensity of exciting light in different regions of the E.S. (Fig. 7).

If one of the maxima in the E.S. is selected for excitation, the intensity of exciton emission I_{em} is proportional to intensity

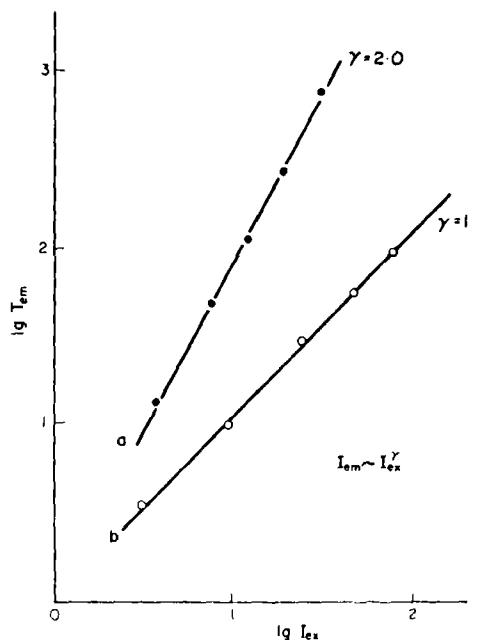


Fig. 7. Dependence of $n = 1.4$ exciton emission line intensity I_{em} on the intensity of exciting light I_{ex} at $T = 77$ K. a—excitation with mercury line $\lambda = 366$ m μ ; b—excitation with the $\lambda = 405$ m μ line.

of the exciting light I_{ex} as $I_{em} \sim I_{ex}^\gamma$. At optical excitation in the region far above the fundamental edge ($\lambda = 366$ m μ) excitons are formed from electron-hole pairs (bimolecular process). In this case the concentration of created excitons is proportional to the product of free electron concentration n and the concentration of free holes p , and may be proportional to I_{ex}^2 . At optical excitation in the spectral region just above the fundamental edge, the exciton formation takes place mainly due to indirect exciton transitions (monomolecular process). The concentration of excitons, created in this process, must be

proportional to the intensity of exciting light I_{ex} .

Thus, it may be concluded that in the spectral region just above the fundamental edge free excitons are formed mainly due to indirect exciton transitions. The absolute maximum of the E.S. of exciton emission is located in this region. On increasing the photon energy the probability of indirect exciton transitions becomes less, and a drop in E.S. is observed. At excitation in a high energy region free excitons are formed from the thermalized electron-hole pairs.

We have managed to observe up to 7 distinct lines in the E.S. of exciton emission. If we assume that photon energy is partly wasted on the formation of one or two LO phonons, the maximum kinetic energy of excitons created in our experiments equals to 0.2 eV. This energy considerably exceeds the ionisation energy of a free exciton in CdS crystals (0.03 eV) and kT value at 77°K (0.01 eV). Thus it may be concluded that in the E.S. of exciton emission we observe the formation of 'hot' excitons.

The appearance of oscillating structure is entirely connected with the absence of thermal quasi-equilibrium in exciton bands. Since the thermalization time can be estimated as being less than 10^{-9} sec in CdS at 4·2°K [9], it must be presumed that in our samples free exciton life-time was of order 10^{-10} sec at 4·2°K. Such short life-time is evidently determined by great probability of nonradiative recombination.*

At rising the temperature exciton thermalization time becomes shorter. Simultaneously the exciton life-time becomes also shorter, which can be concluded from the weakening of free exciton emission from 4·2 to 77°K. Thus, the nonequilibrium distribution of exciton kinetic energies can exist up to rather

high temperatures. Moreover, as our experiments show, the observation of oscillating E.S. for exciton emission is even easier at 77 than at 4·2°K.

The dependence of exciton kinetic energy distribution function on exciton life-time may explain the discrepancy between the results of this work and our previous measurements [7] of equilibrium distribution of exciton kinetic energies in CdS crystals. The samples used for the latter measurements had a high intensity of phonon-assisted exciton emission lines. It may be assumed that free exciton life-time in these samples was long enough for the establishment of thermal equilibrium in the exciton band. Samples used for the present measurements had an intensity of phonon assisted free exciton emission lines 10 to 50 times weaker than in the previous case. This low intensity is evidently connected with the short life-time of free excitons in these crystals.

The observation of non-equilibrium exciton kinetic energy distribution in the E.S. of resonant exciton lines is promoted by the existence of strong self-absorption for these emission lines in the crystals, as explained below.

In the process of optical excitation of a crystal the exciton formation takes place in a rather thin layer near the illuminated surface. The thickness of this layer depends upon the absorption coefficient value in the fundamental region, and is about 10^{-5} cm for CdS crystals. Then a diffusion of the excitons into the bulk of the crystal takes place. It is accompanied by a simultaneous thermalization of excitons.

The further the excitons move inside the crystal, the nearer is their kinetic energy distribution to the equilibrium function determined by the lattice temperature. If the emission, the E.S. of which is studied, is strongly absorbed in the sample, only the radiation, which arises in crystal regions close to the excited surface, will escape the sample and will be detected by the outer receiver. The

*For interpretation of nonequilibrium exciton emission in CuBr Goto and Ueta [31] used polariton dispersion peculiarities near point $K' - 0$ [37]. However, in our experiments the short life-time of free excitons should be assumed for all the points of the exciton band.

distribution of exciton kinetic energies in crystal regions, examined in such experiments, most strongly differs from the equilibrium one, and this non-equilibrium distribution is reflected in the E.S. of observed emission.

Simultaneous observation of zero-phonon emission lines, corresponding to different exciton bands ($n = 1A$, $n = 1B$ and $n = 2A$) in the low temperature spectra of CdS crystals may be also connected with the non-equilibrium character of free exciton zero-phonon emission, caused by a strong resonant self-absorption in the crystal.

5. SUMMARY

The investigation of E.S. of free exciton emission has shown that in many cases the processes of exciton emission are essentially nonequilibrium. Exciton formation under optical excitation occurs most efficiently in the spectral region just above the fundamental edge. In this region excitons are mainly formed due to indirect optical transitions into exciton states. As a result of such transitions LO phonons and excitons with considerable kinetic energy are created. We have observed the formation of excitons with kinetic energy up to 0.2 eV, which considerably exceeds binding energy of free excitons 0.03 eV.

The measurements of exciton emission intensity dependence on the intensity of exciting light has shown that at light absorption in the energy region far above the fundamental edge ($\lambda = 366 \text{ m}\mu$) excitons are formed mainly from the thermalized electron-hole pairs.

We are of an opinion that a critical analysis of these results may be used for determination of such important free exciton kinetic parameters as life-time and diffusion length.

Though the observation of discrete structure in E.S. in our experiments is connected with the nonequilibrium character of relaxation processes in the samples studied, our results concerning the processes of exciton formation under optical excitation should be

valid for CdS crystals with any free exciton life-time.

REFERENCES

1. GROSS E. F. and KARRIEV N. A., *Dokl. Akad. Nauk USSR* **84**, 261, (1952)
2. KNOX R., *Theory of excitons* Academic Press, New York (1963)
3. MOSKALENKO S. A., *Fiz. tverd. Tela* **4**, 276, (1962)
4. KELDYSH L. V. and KOZLOV A. I., *Zh. eksp. Teor. Fiz.* **54**, 978, (1968)
5. ASNIN, V. M., ROGACHEV A. A. and RYVKIN S. M., *Soviet Phys. Semicond.* **1**, 1742, (1967)
6. HAYNESS J. R., LAX M. and FLOOD W. F., *Proc. Int. Conf. Semicond. Prague*, p. 423 (1960).
7. GROSS E., PERMOGOROV S. and RAZBIRIN B. J., *Phys. chem. Solids*, **27**, 1647, (1966).
8. VOJGT J. and SPIEGELBERG F., *Phys. Status Solidi* **30**, 659, (1968).
9. SEGALL B. and MAHAN G. D., General Electric Information Reports, Technical Series No 68-C-053
10. MAHAN G. D. and SEGALL B., BIEHL C. E. and GAY J. G., FAIT W. C., CAMPBELL D. A., PACKARD J. R. and WEIHER R. L., in *Proc. Int. Conf. II-VI Semicond. Comp.* p. 349 W. A. Benjamin, New York (1967)
11. GROSS E. F. and SCHECHMAMETIEV R. I., *Fiz. tverd. Tela* **3**, 3162, (1961)
12. DEVORE H. B., *Phys. Rev.* **102**, 86 (1956)
13. TITOV R. A., *Soviet Phys. Semicond.* **1**, 217 (1967)
14. STOCKER H. J., STANNARD C. R., KAPLAN P. J., *Phys. Rev.* **161**, 762 (1967)
15. DENHAM P., TIGHTOWERS F. C., DEAN P. J., *Phys. Rev.* **161**, 762 (1967)
16. STOCKER H. J. and KAPLAN H., *Phys. Rev.* **150**, 619, (1966) CORET A., RINGFELT N. Y., NIKHINE S., *Solid State Commun.* **5**, XVI (1967).
17. DEAN P. J. and MALE J. C., *Proc. R. Soc.* **A277**, 330 (1964)
18. DEAN P. J., *Phys. Rev.* **168**, 889 (1968)
19. PARK Y. S. and SCHNEIDER H., *Phys. Rev. Lett.* **21**, 798, (1968)
20. BROUDE V. I. and MEDVEDEV V. S., *Izv. Akad. nauk USSR, fiz.* **25**, 430, (1961)
21. CONRADI J. and HAERING R. R., *Phys. Rev. Lett.* **20**, 1344, (1968)

27. THOMAS D. G. and HOPFIELD J. J., *Phys. Rev.* **116**, 573, (1959).
28. GROSS E. F. and RAZBIRIN B. S., *Fiz. tverd. Tela* **4**, 207, (1962).
29. GROSS E. F., RAZBIRIN B. S. and PERMOGOROV S. A., *Dokl. akad. Nauk USSR* **147** 338 (1962).
30. GROSS E. F., ILYINSKII A. V., LIEDER K. F., NOVIKOV B. V. and SOKOLOV N. S., *Phys. Status Solidi* **34**, K59, (1969).
31. GOTO T. and UETA M., *J. phys. Soc. Japan* **22**, 488 (1967).
32. STEPANOV B. I., Luminescence of complex molecules. Moscow (in Russian) (1955).
33. ANSELM A. I. and FIRSOV Yu. A., *Zh. eksp. Teor. Fiz* **28**, 151 (1955); **30**, 719 (1956).
34. SEGALL B., *Phys. Rev.* **150**, 734, (1966).
35. SEGALL B. and MARPLE R., *Phys. Rev.* **156**, 850 (1966).
36. THOMAS D. G., HOPFIELD J. J. and POWER M., *Phys. Rev.* **119**, 570 (1960).
37. LIPNICK A. A., *Fiz. tverd. Tela* **6**, 1068 (1964).
38. HOPFIELD J. J., *Phys. Rev.* **112**, 1555 (1958).

SURFACE IMPEDANCE OF GOLD FILMS ON BULK SUPERCONDUCTING TIN*

H. A. COMBET

Centre National d'Etudes des Télécommunications, 22-Lannion France

(Received 8 December 1969; in revised form 6 March 1970)

Abstract—We have studied experimentally the variations of the surface impedance at 4 GHz of gold films evaporated on bulk tin, as a function of temperature and gold thickness. The results for surface resistance agree with a recent theory by Hurault on non-local effects in the electromagnetic response of superconducting contacts. The data for surface reactance show the phenomenon of anomalous penetration predicted by De Gennes and Matricon. The values of the surface impedance when the tin is in the normal state, used to normalize the data, are derived from a theory by Meissner predicting a 'normal state proximity effect'. The consistency of the experimental results gives a check of all theories.

1. INTRODUCTION

IN THE present study, we have measured the variations with the temperature of the surface impedance, at a frequency of about 4 GHz, of gold films evaporated on bulk tin crystals. We were mainly concerned with the superconductivity induced in the normal metal gold by its proximity with superconducting tin, and with the influence gold has on superconductivity in tin. The electrodynamic properties of superconducting contacts have already been extensively studied in Refs. [1-5]. We investigated the following properties: (a) surface resistance as a function of thickness, in order to check a recent theory by Hurault[2,3] predicting non-local effects in the electromagnetic response of superconducting contacts; (b) surface reactance, to evidence the phenomenon of anomalous penetration predicted by De Gennes and Matricon[6]. As far as we know, this effect was born out only by low frequency experiments[7] or indirectly, at microwave frequencies when measuring surface resistances in a magnetic field[5].

As we measured only surface impedance variations, we needed to compute the surface

impedance when tin is in the normal state. We used a theory by Meissner[8] predicting a kind of 'normal state proximity effect'.

At first let us recall some useful theoretical results. The geometry of the system is shown on Fig. 1.

$$Z_s = R_s + iX_s = \frac{1}{ch} \frac{1}{K} \frac{d_N}{d_A}$$

where K is given by [9]

$$\text{Log} \frac{T_{cN}}{T} = \Psi\left(\frac{1}{2} - \frac{\hbar D_N K^2}{4\pi K_B T}\right) - \Psi\left(\frac{1}{2}\right) \quad (2)$$

D_N being the diffusion coefficient in N ; $D_N = \frac{1}{2} v_F \lambda_N$, v_F being the Fermi velocity and λ the mean free path. T_{cN} is the critical temperature of gold. If we assume $T \ll T_{cN}$, (2) reduces to

$$K^{-1}(T) = \left(\frac{\hbar v_F \lambda_N}{6\pi K_B T}\right)^{1/2} \quad (3)$$

*Partially supported by the Direction des Recherches et Moyens d'Essais

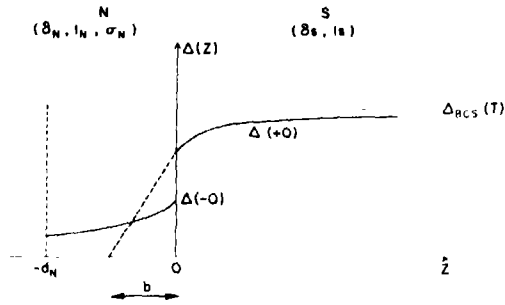


Fig. 1. Schematic representation of the pair potential.

and taking $v_{F_N} = 1.4 \cdot 10^8$ cm/sec [10]

$$K^{-1}(T) = 58 \left(\frac{1}{T} \right)^{1/2} (1/\text{\AA}), \quad K^{-1} \text{ in } \text{\AA}, \quad T \text{ in } ^\circ\text{K}. \quad (4)$$

Inside *S* (index *S*) we get [11]:

$$\Delta(+0) = \Delta_{NCS}(T) \frac{1}{\sqrt{2}} \left[\sqrt{2 + \frac{1}{(bq)^2}} - \frac{1}{bq} \right] \quad (5)$$

where *q* is given by

$$\log \frac{T_{CS}}{T} = \Psi \left(\frac{1}{2} + \frac{\hbar D_S q^2}{4\pi K_B T} \right) - \Psi \left(\frac{1}{2} \right). \quad (6)$$

The extrapolation length *b* is given by:

$$b = \frac{D_S N_S}{D_N N_N} K^{-1} \coth K d_N \quad (7)$$

N_N , being the respective densities of states at Fermi levels. In the limit $T \rightarrow T_{CS}$, q^{-1} is given by

$$\lim_{T \rightarrow T_{CS}} q^{-1} = 0.85 (\xi_0 l_N)^{1/2} \left(1 - \frac{T}{T_{CS}} \right)^{-1/2} = \xi_S(T) \quad (8)$$

(ξ_0 BCS coherence length).

Equation (5) predicts a decrease of the pair potential in tin near the *N-S* boundary. The corresponding increase in the penetration depth has been computed in [6] where the ratio of the effective penetration depth λ_{eff} to

$\lambda(T)$ is given as a function of $\eta = [\xi_S(T)]/b$ and of the Ginzburg-Landau parameter κ of the material.

(b) Normal state proximity effects

We make the following hypotheses to compute the surface impedance of the plated sample when tin is in the normal state:

(1) extreme anomalous skin effect in tin. For a semi-infinite sample, the surface impedance may be written:

$$Z_{Sn} = \mu_0 \omega \frac{\delta_S}{2} (1 + j\sqrt{3}) \quad (9)$$

(the anomalous skin depth δ_S is about 2300 Å at 4.1 GHz)

(2) normal skin effect in gold: for a semi-infinite material we would get:

$$Z = \mu_0 \omega \frac{\delta_N}{2} (1 + j) \quad (10)$$

with

$$\delta_N = \left(\frac{2}{\mu_0(T_N \omega)} \right)^{1/2}. \quad (11)$$

If we take $Z_0 = (Z_{Sn}/Z)$, the surface impedance of the plated material is easily shown to be [4]:

$$Z_{\text{eff}} = Z \frac{(Z_0 + 1) + (Z_0 - 1) e^{-2(1+j)d_N/\delta_N}}{(Z_0 + 1) - (Z_0 - 1) e^{-2(1+j)d_N/\delta_N}} \quad (12)$$

or, taking $x = (\delta_N/d_N)$ and $y = (\delta_S/d_N)$

$$Z_{\text{eff}} = \mu_0 \omega \frac{d_N}{2} [r_{\text{eff}}(x, y) + j x_{\text{eff}}(x, y)] \quad (13)$$

r_{eff} and x_{eff} being two real functions of *x* and *y* we have tabulated.

Using the precedent analysis and a model of free electrons, Meissner[4, 8] has shown that the effective microwave conductivity σ_{eff} of gold (to be used instead of σ_N in equation (11)) is given by:

$$\frac{\sigma_{\text{eff}}}{\sigma_N} = 1 + \left[\frac{\delta_N}{2d_N} - \frac{1_N}{4d_N} \right]$$

$$\log \frac{1 + \alpha(1_S/1_N)}{1 + \alpha(1_S/1_N) \exp(-4d_N/1_N)} \quad (14)$$

$\alpha \leq 1$ being the probability for electrons to travel from tin to gold, without suffering diffusion (experimentally $\alpha(1_S/1_N) \sim 10^2$ so that α is not negligible). If the electrical contact between tin and gold is bad ($\alpha \rightarrow 0$), $\sigma_{\text{eff}} = \sigma_N$, so that we may really speak of a 'normal state proximity effect'.

If $d_N < 1_N$, (14) reduces to

$$\frac{\sigma_{\text{eff}}}{\sigma_N} = \frac{2\delta_N}{1_N} \quad (15)$$

A more refined treatment, using the Boltzmann equation, yields a formula analogous to (15) in the same limit $d_N < 1_N$ [12].

Equations (11) and (15) show that x and y are related by

$$yx^2 = \frac{1}{\mu_0 \omega d_N} \left(\frac{1_N}{\sigma_N} \right) \quad (16)$$

or taking numerical values for gold at GHz [4, 8]

$$yx^2 \sim 37.5 \left[\frac{10^3}{d_N} \right]^3 (d_N \text{ in } \text{\AA}). \quad (17)$$

Our procedure to compute the normal state surface impedance of the plated sample is then straightforward: d_N and y are known; from (17) or from the equivalent formulas deduced from (11) and (14) when $d_N > 1_N$, we compute x ; then we finally use (13) and the tabulated values of $r_{\text{eff}}(x, y)$ and $x_{\text{eff}}(x, y)$. The results are not very sensitive to the exact value of $\alpha(1_S/1_N)$ [8]. We take $\alpha(1_S/1_N) = 10^2$.

2. EXPERIMENTAL METHODS

(a) Measuring technique

We use a reflexion spectrometer (or precision Smith Chart plotter) with a rutile dielectric cavity at a frequency of about 4 GHz ($h\nu/(K_B T_C) \approx 5 \times 10^{-2}$). The experimen-

tal set-up is analogous to those already used by Dresselhauss and others [13] and Glosser [14] for the measurement of surface impedance of superconductors. The principle is described at full length by Kyhl [15]. What we measure are the variations of the reflection coefficient Γ of the rutile cavity placed upon the sample, as a function of temperature.

The reduced impedance z of the cavity, found on the Smith Chart as in [14] can be written

$$z = r + jx = Q_c \left[K(R_b + R) + j \left(\frac{2\Delta\omega}{\omega_0} + KX \right) \right] \quad (18)$$

where Q_c : coupling surtension coefficient

$R + jX$: surface impedance of the sample

R_b : resistance equivalent to the dielectric losses in rutile

K : coefficient depending upon the exact mode of the resonator

$\frac{\Delta\omega}{\omega_0} = \frac{\omega - \omega_0}{\omega_0}$ pulsation dissonance

Starting from $I_0 \approx I_{c_{\text{N}}$ and a tuned cavity and lowering T through $T_{c_{\text{N}}}$ we find the variations

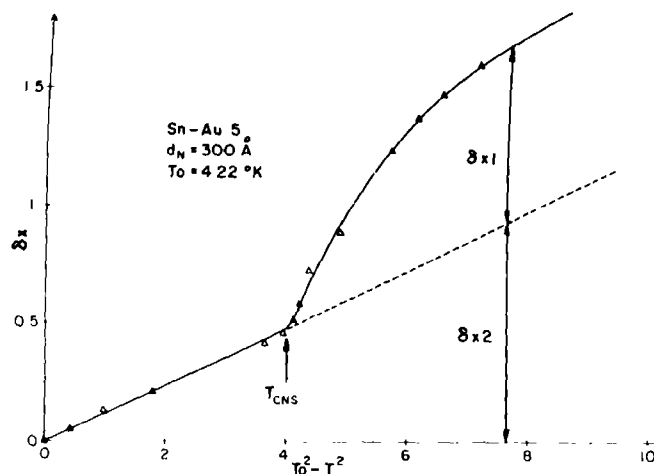
$$\delta z = z - z_0 - \delta r + j(\delta x_1 + \delta x_2) = Q_c K (R - R_b) + jQ_c K (X - X_0) + 2jQ_c \delta \left(\frac{\Delta\omega}{\omega_0} \right) \quad (19)$$

δx_2 is due to the variations of the dielectric constants of rutile with T (for $T \approx 4.2^\circ\text{K}$, the dielectric losses do not vary appreciably). The two dielectric constants ϵ and ϵ' having a parabolic variation with T in that range, a plot of δz versus T yields two parabolas, one for ϵ and one for ϵ' .

As stated by Lanelli's results [4] the limits $R_b/R_0 \approx 10$ per cent for $d_N \approx 1000 \text{\AA}$ at 9 GHz. Anyway, we can certainly neglect the systematic error introduced by that assumption as long as $R/R_0 > 50$ per cent.

(b) Sample preparation

Two plates (dia. 20 mm, thickness: 4 mm) were spark cut with the same orientation from the same zone of a crystal grown from 99.999 per cent pure tin (Hoboken). In order to avoid any anisotropy effect only these two plates were used for all samples. The plates were electropolished in order to remove the perturbed surface layer. Just after the final touch of polishing, a plate was mounted in a vacuum jar. Gold was evaporated on the plate held at ambient temperature (pressure during evaporation $5 \cdot 10^{-6}$ torr). After evaporation, samples were kept at 77°K before mounting in the spectrometer. After completion of a run, gold was dissolved and the procedure repeated.

Fig. 2 Reduced cavity reactance δx vs. $T_0^2 - T^2$.

The thickness of the gold layer is measured by classical interferometrical methods on the samples and on test layers evaporated on glass slides at the same time. $M/\rho \cdot l_N$ is deduced as usual, from the residual resistivity ratio (R/R_R) of the test samples. We find $l_N = 240 \text{ \AA}$ independently of d_N .

The problem of interdiffusion between gold and tin has already been discussed in [4]. Nevertheless, we may note the following points: X-rays diffraction patterns of samples aged during two months at room temperature did not reveal the formation of intermetallic compounds. This contrasts with the results of Klokholm[19] for thin tin films. Moreover, as pointed out by Meissner[8], if they existed, the compounds should have the same value of $1/\alpha$ as pure gold. Diffusion effects exist, as shown on Fig. 3, the critical temperature T_{CNS} decreases with increasing d_N . This cannot be explained by proximity effects, but can be due to the lowering of l_N by diffusion of gold into tin. The general m/ρ effect on T_c for alloys of various solutes into tin has been studied by Serin and coworkers[20]. Using their general relation between the fractional change in T_c and ξ_0/l_N for electropositive solutes, we get an estimation of l_N . For $d_N = 1000 \text{ \AA}$ we find $\xi_0/l_N = 0.7$. Since numerically $\xi_0 = 2300 \text{ \AA}$, we still have a very anomalous skin effect in tin (see 1(B)). This agrees with the fact that the assumption of a normal skin effect does not lead to consistent results for the surface reactance (see below).

Moreover, Duffy[16] was able to reverse the decrease in T_{CNS} of Sn-Au contacts evaporated at room temperature by dissolving some of the gold. This rules out diffusion effects as the only interpretation of the observed phenomena. On the other hand, since our gold films are already dirty, diffusion of tin into gold is not meaningful.

Since we must also assume that $\sigma_{\text{eff}} \neq \sigma_N$ for the consistency of the surface reactance data, the possible oxide layer on tin does not play a significant role. Unfortunately, the theory is not sensitive to the exact value of $\alpha(1/l_N)$, so that we cannot determine α and l_N separately.

3. EXPERIMENTAL RESULTS AND DISCUSSION

(a) Surface resistance

The values of the surface resistance of our samples, normalized as described above, are plotted vs. $t = (T/T_{CNS}(d_N))$ on Fig. 3. For the sake of clarity, the curve for unplated tin is omitted. It does not differ very much from the curve corresponding to $d_N = 150 \text{ \AA}$.

Figure 4 shows the variations of $\rho(t, d_N) = 1 - (R/R_0)$ vs d_N . ρ is normalized to the value for unplated tin corresponding to the same reduced temperature (using $T_{CNS}(0) = 3.72 \text{ °K}$) (this eliminates the dispersion in T_{CNS}^*).

The full curve is a best fit to the function $f(Kd_N)$ where $f(u) = (u^2 + sh^2 u/2u^2 ch^2 u)$ is deduced from Hurault's theory as explained in the Appendix. From the fit, we deduce $K^{-1}(T_{CNS}) = 450 \text{ \AA}$ and from (4), $l_N \sim 220 \text{ \AA}$ in agreement with values deduced from $R.R.R.$ measurements (see Section 2(b)).

The decay of ρ as $(Kd_N)^{-2}$ when $Kd_N > 1$ is emphasized on Fig. 5. For $t \approx 0.98$ and small d_N values, we are already out of the range of validity of the theory which uses

* The absolute error in the determination of T_{CNS} is 0.01°K , but the temperature variations in a given run are more accurately known, and the precision on t is better than 10^{-3} .

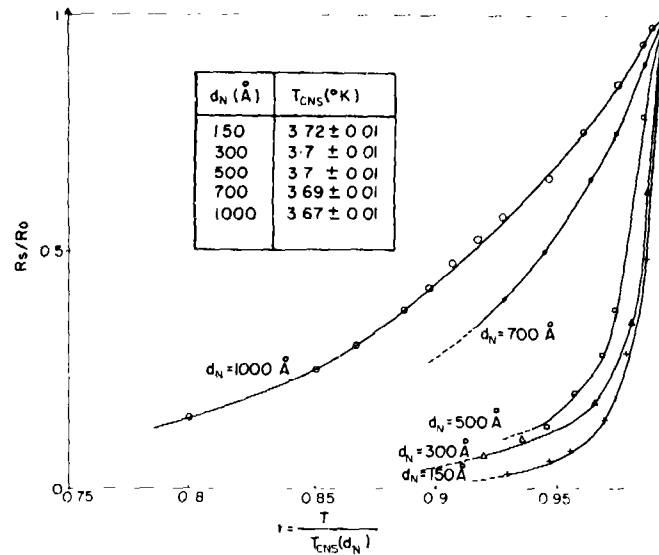


Fig. 3. Normalized surface resistance vs. reduced temperature and gold thickness.

developments in powers of Δ , but we still find a d_N^{-2} dependance for large d_N .

The fit is obtained though the hypothesis of a dirty S material is not verified (the above discussion shows that it is not very clean). Anyway, any function $f(u)$ such as $f(0)$ and $f(u) \sim \frac{1}{2}u^2$ if $u \rightarrow \infty$ would give ne such a good fit.

(b) Surface reactance

Our measurements give the imaginary part of the penetration depth $\delta_{iS} = X_S/\mu_0\omega$. In order to compare it with the effective penetration depth $\lambda_{eff}(T)$, we should make corrections according to the Kramers-Kronig relation[17]:

$$\delta_{iS}(\omega, T) - \lambda_{eff}(T) = \frac{2\omega^2}{\pi^2} \int_0^\infty \frac{\delta_{iS}(\omega', T) d\omega'}{\omega'(\Omega'^2 - \omega^2)}. \quad (22)$$

Unfortunately, $R_S = \mu_0\omega\delta_{iS}$ has not been extensively measured as a function of frequency for plated materials. Anyway these corrections have been done by Waldram[17]

for unplated tin. From his results, we may admit that at 4 GHz:

$$\delta_{iS}(T) = T - 3.6(T - T_{cNS})^2$$

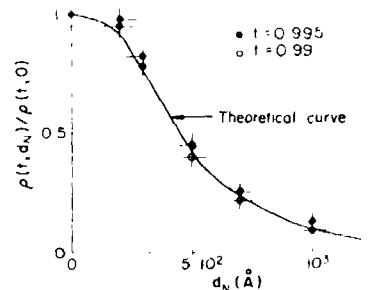


Fig. 4 $\rho(t, d_N)/\rho(t, 0)$ vs. d_N with $\rho = 1 - R_S/R_0$. The theoretical curve is a best fit to Hurault's theory (see Appendix)

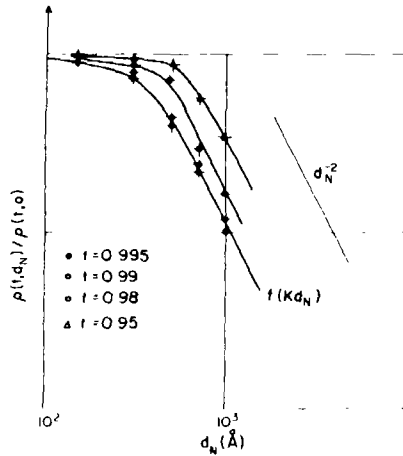


Fig. 5. $\rho(t, d_N)/\rho(t, 0)$ vs. d_N , 1 logarithmical coordinates

unplated tin for which our results agree with [17]. η is deduced from (7) and (8) using numerical values of N and v_F for gold and tin [16] and the 1_s and K^{-1} values found previously. As 1_s is not precisely known, we use the trick of taking the largest *m.f.p.* compatible with the theory i.e. $1_s = \xi_0$ (the same approximation is done in [5]). The theoretical curve is computed from [6]. It is parametrically defined by:

$$\frac{\lambda_{\text{eff}}}{\lambda(T)} = -\frac{1}{m} \frac{A(\theta)}{dA/d\theta} \quad (23)$$

and

$$\eta = \frac{1}{\sqrt{2}} \frac{1 - th^2\theta}{th\theta} \quad (24)$$

where

$$A(\theta) = \frac{1}{ch^{1/m}\theta} F\left(-\frac{s}{2} + \frac{1}{2m}, \frac{1}{2} + \frac{s}{2} + \frac{1}{2m}, 1 + \frac{1}{m}, \frac{1}{ch^2\theta}\right) \quad (25)$$

$F(\alpha, \beta, \gamma, z)$ being a hypergeometrical function with:

$$s = \frac{1}{2} \left(-1 + \sqrt{1 + \frac{4}{m^2}} \right) \text{ and } m = \frac{\kappa}{\sqrt{2}} = 0.114$$

(we neglect the variation of κ with T).

We may do the following comments:

(a) We used the D.G.W. theory for a clean superconductor, with $l_s = \xi_0$.

In the absence of theories pertaining to our experimental situation, we may get an idea of the uncertainty in the η values found above by comparing the values one would get for two semi-infinite materials:

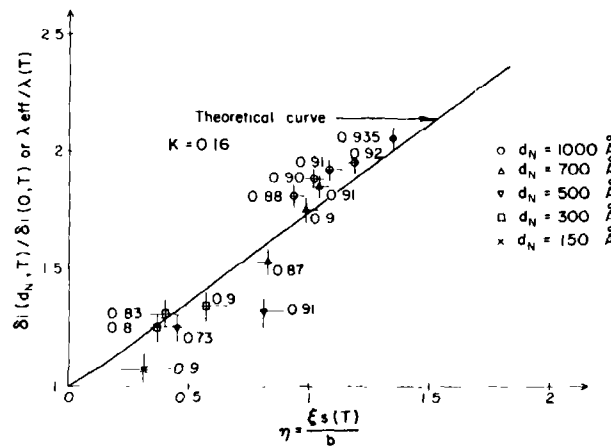


Fig. 6. Anomalous penetration depth $\delta_N(d_N, T)/\delta_N(0, T)$ vs. $\eta = \xi_s(T)/b$, for different d_N and t . Theoretical curve according to Ref [6] (see text)

—D.G.W. theory for dirty identical materials:

$$b = K^{-1} \text{ and } \eta = 1.57 \sqrt{\frac{t}{1-t}} \quad (26)$$

—Zaitsev theory [18] for clean materials differing only by the BCS interaction V with $V_N = 0$:

$$b = \frac{\xi_0}{\sqrt{2}} \text{ and therefrom } \eta = \frac{1.03}{\sqrt{1-t}} \quad (27)$$

(26) and (27) do not differ by more than about 50 per cent for $t > 0.7$.

(b) Corrections due to the finite frequency used may compensate because of the normalisation to $\delta_N(0, T)$.

(c) For most thicknesses, $\eta \sim 1/bq \ll 1$ so the approximation $\Delta(+0) = \Delta_{BCS}(T)$ used for computing ρ in the Appendix is not too bad.

(d) In all the theoretical calculations, the inequality $d_N \ll \delta_N$ is supposed to hold: in fact our values of δ_N , deduced from (17) or equivalent formulae, range from $\delta_N = 3750 \text{ \AA}$ for $d_N = 150 \text{ \AA}$ to $\delta_N = 6000 \text{ \AA}$ for $d_N = 1000 \text{ \AA}$.

4. CONCLUSIONS

The preceding results are in rather good agreement with the theories to which they are compared. The non-local character of the electromagnetic response of superconducting contacts is well born out by the decay of ρ as d_N^{-2} for large d_N . We have obtained also a microwave evidence of the anomalous penetration phenomenon. We lack a determination of I_s , but we nevertheless obtain a more accurate check of Meissner's theory than his calorimetric experiments, but still on the same Au-Sn system.

Acknowledgements—The author would like to thank Dr. J. P. Hurault and the members of the Orsay Group for numerous stimulating discussions. He thanks also Mr. J. P. Meunier and Y. Chouan for their most valuable help in performing the experiments.

REFERENCES

1. DEUTSCHER G. and De GENNES P. G., *Superconductivity* (Edited by R. D. Parks), Marcel Dekker New York (1969).
2. DEUTSCHER G., HURAUULT J. P. and VAN DALEN P. A., *J. Phys. Chem. Solids* **30**, 509 (1969).
3. HURAUULT J. P., Ph.D. Thesis Orsay 1968 Unpublished.
4. FANELLI R. and MEISSNER H., *Phys. Rev.* **147**, 227 (1966) and Final Report on ONR Contract Nonr 263 (32) 1964 (Unpublished).
5. FISCHER G. and KLEIN R., *Physics condensed Matter* **7**, 12 (1968).
6. De GENNES P. G. and MATRICON J., *Solid State Commun.* **3**, 151 (1965).
7. DEUTSCHER G., *J. Phys. Chem. Solids* **28**, 741 (1967).
8. MEISSNER H., *Phys. Rev.* **147**, 235 (1966).
9. De GENNES P. G. and GUYON E., *Phys. Lett.* **3**, 168 (1963).
10. KITTEL C., *Introduction to Solid State Physics*, p. 250, Wiley, New York (1956).
11. GUYON E., MARTINET A., MAURO S. and MEUNIER F., *Phys. condensed Matter*, **5**, 123 (1966).
12. COMBET H. A., Unpublished work.
13. DRESSELHAUSS M. S., DOUGLASS D. H. and KYHL R. L., In *Proc. of the 8th Int. Conf. on low temp. Phys. London 1962* (Edited by R. O. Davies), Butterworth, London (1963).
14. GLOSSER R., *Phys. Rev.* **156**, No. 2, 500 (1967).
15. KYHL R. L., *Rev. scient. Instrum.* **39**, 373 (1968).
16. DUFFY R. J. and MEISSNER H., *Phys. Rev.* **147**, 211 (1966).

Hurault [2, 3] has calculated the surface impedance from the relation:

$$J(z) = -Q(z, \omega) A(z, \omega) \quad (A1)$$

If $\delta Q(z, \omega)$ is the part of $Q(z, \omega)$ which is proportional to Δ^2 we have in Λ :

$$\delta Q(z, \omega) = \delta Q(0, \omega) \frac{\cosh^2 K(z + d_N)}{\cosh^2 K d_N} \quad (A2)$$

We may replace $\delta Q(z, \omega)$ by an average value $\delta \bar{Q}$ such that

$$\delta \bar{Q} = \frac{\int_{d_N}^{\Lambda} \delta Q(z, \omega) A_0(z) dz}{\int_{d_N}^{\Lambda} A_0(z) dz} \quad (A3)$$

$A_0(z)$ being the vector potential in the system for $T \approx T_{cvs}$, using BCS formulas

Assuming $D_S \gg D_N$, we may neglect the attenuation in N and the penetration in S , then $A_0(z) \sim z$.

Injecting (A2) in (A3) we find,

$$\delta Q = \delta Q(0, \omega) f(K d_N) \quad (A4)$$

where

$$f(u) = \frac{u^2 + \chi h^2 u}{2u^2 \epsilon h^2 u} \quad (A5)$$

Following Hurault, and neglecting small terms, the surface impedance is then:

$$R_N = R_0 \left[1 - \frac{\pi}{4} \frac{\Delta^2}{h\omega K_H T} \right] \quad (A6)$$

$$X_N = X_0 \left[1 + \frac{\pi}{4} \frac{\Delta^2}{h\omega K_H T} \right] \quad (A7)$$

where

$$\Delta^2 = \Delta^2(+0) f(K d_N) \quad (A8)$$

$\Delta(+0)$ depends on d_N through (5) and (7); however, as $D_N \gg D_N$, the dependance is rather weak. The ratio $\rho = (R_0 - R_N(t)/R_0)$ will then depend upon d_N as $f(K d_N)$.

Formulae (A6) and (A7) are reminiscent of the follow-

and

$$\frac{R_N}{R_0} = 1 - \frac{\sigma_2}{2\sigma_0} \quad (A9)$$

$$\frac{X_N}{X_0} = 1 + \frac{\sigma_2}{2\sigma_0} \quad (A10)$$

with

$$\frac{\sigma_2}{\sigma_0} = \frac{\pi \Delta_{BCS}^2(T)}{2 h\omega K_H T} \quad (A11)$$

to which they reduce if $d_N \rightarrow 0$. Their range of validity is the same and is very small for clean superconductors [2, 3]. However, out of that range, the functional dependance on d_N , should not be drastically modified. Moreover, as long as $\sigma_2/\sigma_0 \ll 1$, (A9) is a good approximation over a large range of temperatures to the formula deduced from a local two fluids model:

$$\frac{R_N}{R_0} = \left[\frac{(1 + (\sigma_2^2/\sigma_0^2))^{1/2} - (\sigma_2/\sigma_0)}{1 + (\sigma_2^2/\sigma_0^2)} \right]^{1/2} \quad (A12)$$

That is not true of the corresponding formulas for X_N/X_0 , so we did not try to verify (A7). (The predicted rise of X_N/X_0 just below T_c has nevertheless been evidenced for tin [17]).

INHOMOGENEOUS BROADENING OF THE OPTICAL SPECTRA OF Yb^{3+} IN PHOSPHATE GLASS

J. T. FOURNIER

Central Research Laboratory, American Optical Corporation, Southbridge, Mass. 01550, U.S.A.

and

R. H. BARTRAM

Physics Department and Institute of Materials Science, University of Connecticut, Storrs, Conn 06268, U.S.A.

(Received 9 February 1970)

Abstract—The observed widths and asymmetries of the spectral lines of Yb^{3+} in phosphate glass are attributed to systematic site-to-site variations in the crystal field at the rare earth. A model rare earth site consisting of a Yb^{3+} ion coordinated by three PO_4 tetrahedra is considered. A compliant mode of distortion of the complex is identified, and it is shown that a distribution of distorted sites can lead to lineshapes which reproduce many of the features of the observed spectra. Using a point-ion model, the crystal field at the rare earth site is calculated as a function of a single configuration coordinate which describes the distortion. The electrostatic energy of the complex is also determined as a function of the configuration coordinate, and the lineshapes are computed from the crystal-field levels assuming a Boltzmann distribution. Because of uncertainty in the structural parameters of the glass, the effect on the lineshapes of variations in the dimension of the complex and in the charge states of the ligands is considered. The crystal-field parameters are scaled to compensate deficiencies in the point ion approximation, and the effect on the lineshapes of changes in the scale factors is discussed.

1. INTRODUCTION

RECENTLY, Robinson and Fournier have inferred a trigonally distorted octahedral site for Yb^{3+} in phosphate, silicate and germanate glasses from a study of the low temperature absorption and emission spectra of the Yb^{3+} ion [1,2]. They propose that the rare earth ion is coordinated by three MO_4 ($M = \text{P, Si or Ge}$) tetrahedral ligands. Two of the oxygen ions associated with each tetrahedron are assumed to be non-bridging ions forming ionic bonds with the rare earth. The other two oxygen ions associated with a tetrahedron are assumed to be bridging oxygens forming the usual $M-O-M$ bonds which link glass-forming tetrahedra. Consideration of ion sizes shows that the Yb^{3+} is too large to permit the six non-bridging oxygens to form an undistorted octahedron if O—O distances appropriate to unaltered glass-forming tetrahedra are maintained. Since covalent bonding strongly favors preservation of the MO_4 geometry, large

distortions

arrayed non-bridging oxygen ions around each of the three tetrahedra through equal distances along the three two-fold axes of the octahedron as shown in Fig. 1.

The absorption and emission spectra of Yb^{3+} in a lanthanum-metaphosphate glass are shown in Fig. 2. The $4f^{13}$ ground configuration of Yb^{3+} gives rise to $^2F_{7/2}$ and $^2F_{5/2}$ levels which are separated by about $10,500\text{ cm}^{-1}$ with the $J = 7/2$ level lying lowest. The J -levels are split through interaction with the crystal field, and transitions involving the maximum allowed number of Kramers doublets are observed. An energy-level diagram

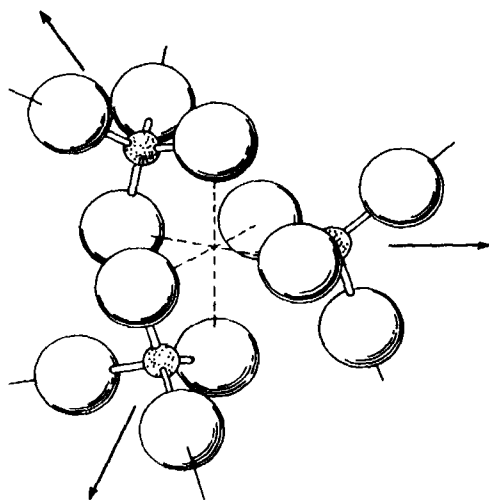


Fig. 1 Proposed rare earth site model. In a structure based on undistorted MO_4 tetrahedra with octahedrally arrayed non-bridging oxygens, the central void of the complex can accommodate an ion with ionic radius about half that of a trivalent rare earth ion. Expansion of the void by translation of the three MO_4 tetrahedra along the three C_2 axes shown by arrows preserves the trigonal symmetry of the complex.

derived from the peak positions is shown in Fig. 3. In this figure, the crystal-field-split levels are labeled according to the octahedral manifolds from which they are assumed to derive [1,2].

Notable features of the spectra are the widths and asymmetries of the component lines. The asymmetries are particularly evident in the absorption spectrum which is more clearly resolved than the emission. In this article, these spectral features are attributed to systematic distortions of the complex described above. This model is based on the assumption that the principal Yb^{3+} spectra arise from a single type of rare earth site. It is assumed also that the covalently bonded PO_4 tetrahedron is the prime structural unit of the glass. Because lattice vibrations are weakly coupled to the $4f$ electrons of the rare earths, it is usually the case that only zero-phonon lines are observed in rare earth spectra. For the case of Yb^{3+} in glass, the negligible Stokes

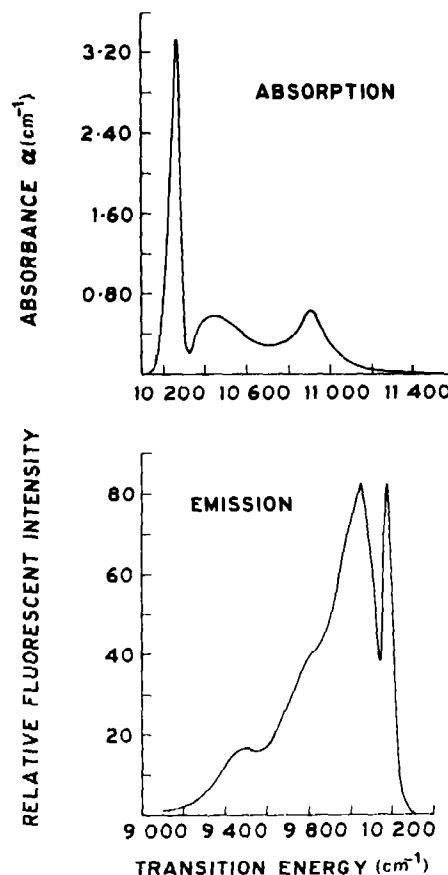


Fig. 2 Absorption and emission spectra of Yb^{3+} in lanthanum-metaphosphate glass at approximately 20°K. The absorption sample contained 1.3 wt.% Yb^{3+} . The sample used for the emission study contained 6.9 wt.% Yb^{3+} and 1.7 wt.% Nd^{3+} to sensitize the ytterbium emission.

shift of the emission is evidence of this [1,2]. Consequently, the source of the lineshapes is sought in variations in the crystal field alone.

In the following sections a compliant distortion of the proposed site model is identified, and it is shown that a distribution of distorted sites can produce lineshapes which reproduce many of the features of the observed spectra. The calculations involve application of crystal-field theory to the model complex. Using a point-ion approximation, the crystal field at the rare earth site is calculated as a

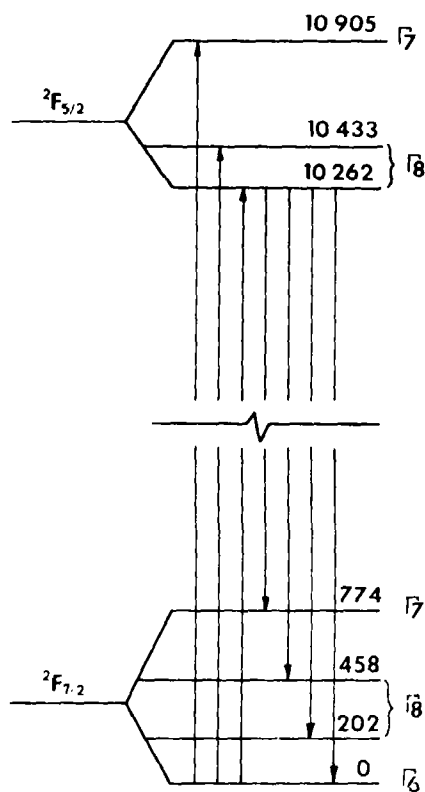


Fig. 3. Energy-level diagram derived from the optical spectra of Yb^{3+} . The crystal-field-split levels are listed according to the octahedral manifolds from which they are assumed to derive. All energies are given in cm^{-1} .

function of a single configuration coordinate describing the distortion. The electrostatic energy of the complex is also determined as a function of the configuration coordinate, and the lineshapes are computed from the crystal-field levels assuming a Boltzmann distribution.

2. THE RARE EARTH SITE MODEL

Prerequisite to the crystal-field calculation is the specification of the positions of the ions in the complex. For rigid, undistorted MO_4 tetrahedra a single distance parameter locating the tetrahedron with respect to the rare earth center is sufficient. A convenient choice for this parameter is the Yb-M distance. In the

work reported here, this distance is estimated from a hard sphere model, and the effects of changes in the dimension of the complex are investigated in the course of the calculations. Because of covalent bonding in the MO_4 ligands, it is difficult to specify an appropriate size for the non-bridging oxygens. However, an effective radius equal to half the O—O distance in the MO_4 tetrahedron seems a reasonable upper bound. In lime-phosphate glass, the glass-forming tetrahedron has P—O and O—O distances of 1.57 and 2.56 Å respectively [3]. Of course, some differences in the dimensions of PO_4 tetrahedra in the lanthanum-metaphosphate glass are possible, and the separation between two non-bridging oxygens on a tetrahedron may be somewhat greater than 2.56 Å. Nevertheless, in the absence of concrete data, we employ the lime-phosphate dimensions to infer an effective radius of 1.28 Å for the non-bridging oxygens. Since the ionic radius of Yb^{3+} is about 1.0 Å, each of the three tetrahedral ligands must be translated by 0.6 Å along the two-fold axes shown in Fig. 1 in order to accommodate the

broadening of the optical lines. The particular mode of distortion considered here involves the simultaneous rotation of each of the tetrahedra about the three two-fold axes. To describe this motion quantitatively, it is convenient to take as configuration coordinate the angle γ formed by the intersection of a line through two non-bridging oxygens associated with one of the tetrahedra with the plane bisecting the complex perpendicular to the C_2 axis as shown in Fig. 4. For the dilated complex derived by simple translation from a structure with octahedrally arrayed non-

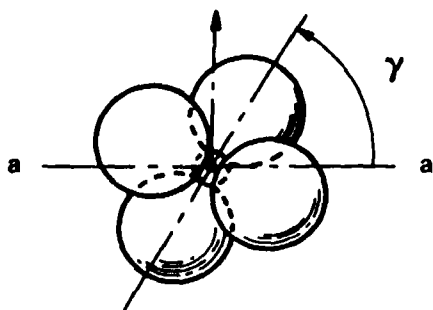


Fig. 4. View of a coordinating PO_4 tetrahedron along a C_2 axis. The configuration coordinate γ is defined by the intersection of a line through the two non-bridging oxygen ions with a horizontal plane perpendicular to the C_2 axis.

bridging oxygens, $\gamma = 55^\circ$. Taking the effective radius of the oxygen ions to be $1.28 \text{ \AA}$, hard sphere contact of non-bridging oxygens on adjacent tetrahedra occurs for γ approximately equal to 30° in the expanded structure. Furthermore, since structures with $\gamma \leq 90^\circ$ are equivalent to structures with configuration coordinate $90^\circ + \gamma$, only configurations in the range $30^\circ \leq \gamma \leq 90^\circ$ need be considered.

Of course, other degrees of freedom exist, and additional modes of distortion could be taken into account. A mode of distortion involving a slipping of the tetrahedra along a spherical surface has been considered, but within the limits determined by hard sphere contact, the effect of such a motion on the crystal field is found to be insignificant. Furthermore, as discussed below, distortions involving expansion or contraction of the complex as a whole are much less compliant than the twisting mode. A more elaborate model incorporating independent twists of the three neighboring tetrahedra could be considered, but, for simplicity, we have arbitrarily constrained the tetrahedra to twist simultaneously. With this restriction, trigonal symmetry is maintained, and a single configuration coordinate can be employed.

To determine the lineshapes resulting from the twisting distortion, the variation of the crystal-field levels with γ and the distribution of centers with respect to the equilibrium

value of the configuration coordinate are required. Since the calculations are to be performed employing a point-ion model, the charges of the ions in the complex must be specified. In the absence of an appropriate molecular calculation of the charge distribution in the PO_4 tetrahedron, we seek to assign charges through application of empirical rules relating the partial ionic character to electronegativity differences. Relationships keyed to various molecular properties have been proposed, and the predicted ionicities can vary widely. In the case of the P—O bond, bounds on the partial ionic character appear to be 40 and 70 per cent [4]. In computing the lineshapes, the charge distribution is regarded as adjustable within this range of ionicities. It is assumed that one electron is transferred from the phosphorous to the non-bridging oxygens and that the remaining four phosphorus valence electrons occupy bonds of fractional ionic character X . The phosphorus charge is therefore $1 + 4X$ in units of electronic charge $|e|$. Bonding of the rare earth to the ligands is taken to be purely ionic, and the three electrons from the Yb^{3+} are distributed equally among the six non-bridging oxygens. Thus the bridging oxygen charge is $-X$ while the non-bridging oxygens carry a charge of $(-X - 1)$.

It is found that increasing the ionicity has the same general effect on the lineshapes as decreasing the size of the complex. Consequently, there are several combinations of charge and size which produce essentially equivalent end results. One such combination is a Yb—P distance of $2.6 \text{ \AA}$ coupled with a charge distribution appropriate to an ionicity of 50 per cent. A plot of the relative electrostatic energy of the complex as a function of γ for this set of parameters is shown in Fig. 5. The curve exhibits a minimum near 49° and is symmetrical about $\gamma = 90^\circ$. To estimate the fraction of centers with a particular value of γ a Boltzmann distribution with characteristic temperature equal to the softening temperature of the glass is employed. For phosphate

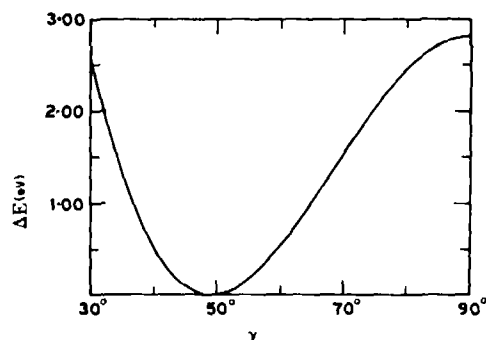


Fig. 5. Relative electrostatic energy of the rare earth complex as a function of the configuration coordinate γ for a Yb—P distance of 2.6 Å and a charge distribution appropriate to a P—O bond ionicity of 50 per cent.

glass, a temperature of about 1000°K is appropriate and $kT = 0.086$ eV. If the probability of finding a site with configuration coordinate γ is denoted by $W(\gamma)$, then $W(\gamma)$ is proportional to $\exp(-\Delta E/0.086)$, where $\Delta E = (E(\gamma) - E(\gamma_0))$ and γ_0 is the equilibrium twist angle. For $(\gamma - \gamma_0) = \pm 6^\circ$, $W(\gamma) \approx 0.01$. Consequently, the major contribution to the lineshapes is expected to come from sites with values of configuration coordinate within a few degrees of equilibrium. For comparison, an increment in the Yb—P distance of about the 2.6 Å value involves changes of about 1.4 eV in the electrostatic energy leading to a corresponding Boltzmann factor of the order of 10^{-7} . Distortions involving expansion or contraction of the complex are much less compliant, and we are led to seek the source of the observed lineshapes in the twisting mode alone.

3. CRYSTAL-FIELD SPLITTING OF THE Yb³⁺ FREE ION LEVELS

In the crystal-field theory, an ion in a solid host is considered to reside in an electrostatic potential $V(\mathbf{r})$ due to all other charges in the material. The form of the potential is restricted by the point symmetry, which is D_3 in the case of the Yb³⁺ site model. In a coordinate system with Z axis along the three-fold

axis and X axis along a two-fold axis, the relevant part of the potential energy of interaction,

$$\mathcal{H}_c = -|e| \sum_i V(\mathbf{r}_i),$$

can be written in the form [5]

$$\begin{aligned} \mathcal{H}_c = & A_2^0 \sum_i (3z_i^2 - r_i^2) \\ & + A_4^0 \sum_i (35z_i^4 - 30r_i^2 z_i^2 + 3r_i^4) \\ & + A_4^3 \sum_i z_i (x_i^3 - 3x_i y_i^2) \\ & + A_6^0 \sum_i (231z_i^6 - 315r_i^2 z_i^4 + 105r_i^4 z_i^2 - 5r_i^6) \\ & + A_6^3 \sum_i (11z_i^3 - 3z_i r_i^2) (x_i^3 - 3x_i y_i^2) \\ & + A_6^6 \sum_i (x_i^6 - 15x_i^4 y_i^2 + 15x_i^2 y_i^4 - y_i^6). \end{aligned} \quad (1)$$

Here, the subscript i denotes electron coordinates. The crystal-field parameters A_l^m are defined by the relationship

$$A_l^m = \frac{1}{(2l+1)!} \left(\frac{d}{d\eta} \right)^m V(\eta),$$

In an earlier section, it was shown that the $^2F_{7/2}$ and $^2F_{5/2}$ levels of Yb³⁺ are separated by about 10,500 cm⁻¹, while crystal splittings of only a few hundred wavenumbers are observed. Consequently, an appropriate description of the effect of the crystal field is

Table 1. Constants k_l^m appearing in equation (2) defining the crystal-field parameters A_l^m

l	2	4	4	6	6	6
m	0	0	3	0	3	6
k_l^m	1/2	1/8	105	1/16	315/2	10,395

obtained by application of $\mathcal{H}_c$ within each J -manifold independently. Evaluation of the required matrix elements of $\mathcal{H}_c$ is accomplished through the use of operator equivalents[6] for the terms of equation (1) in a basis of free ion functions $|4f^{11}, {}^2F; J, M_J\rangle$ which diagonalize J_z . Values of the radial integrals $\langle r^2 \rangle$, $\langle r^4 \rangle$ and $\langle r^6 \rangle$ which occur in the resulting matrix elements are taken from calculations for the free Yb^{3+} ion performed by Freeman and Watson[7].

To determine the variation of the crystal-field levels with configuration coordinate γ , the $A_l^m(\gamma)$ are evaluated, and the matrices $|\mathcal{H}_c(\gamma)|$ are computer diagonalized. With regard to the crystal-field parameters, it is well known that there are serious deficiencies associated with the point-ion approximation. Contributions to a given parameter due to exchange, overlap, covalency, and penetration of the ligand electron clouds are often significant[8]. Shielding and anti-shielding due to the 5s and 5p shells further complicate matters[9]. While no attempt to assess the specific effects of these various interactions is made here, some crude adjustments are made to take into account the results of more thorough treatments of other rare earth systems. In the case of the sixth order parameters, for example, it is found that experimentally deduced parameters are five to ten times larger in magnitude than the point-ion values[10]. The second order parameter A_2^0 falls off slowly with distance, and thus contributions from distant ions are significant. Since effects which depend on overlap of the rare earth charge cloud are less important for ions beyond the first coordination shell, the point-ion contribution is expected to dominate. Although shielding can strongly affect the second order parameter in certain cases[9], the shielding appears to decrease with increasing number of 4f electrons, and should be least effective in Yb^{3+} [12]. The net effect of the various interactions is apparently strongly dependent on the details of the particular case considered. In view of this, our approach has been to investigate the

effect on the lineshape of scaling the crystal-field parameters. In scaling the parameters, it is noted that the calculated ratios A_l^m/A_l^0 are largely independent of the model employed in their evaluation[13]. To the extent that this independence obtains, the computed ratios are valid geometrical parameters. Consequently, scale factors independent of m have been applied.

Crystal field levels for $30^\circ \leq \gamma \leq 90^\circ$ with a rare earth-phosphorus ion distance of 2.6 Å and a charge distribution appropriate to 50 per cent ionicity of the P—O bond are shown in Fig. 6. In Fig. 6(a), the second order parameter is unaltered, the fourth order parameters are scaled by a factor of two, and the sixth order parameters are scaled by a factor of ten. As can be seen from Fig. 6(b), if all scale factors are reduced to unity (i.e. no scaling of the point ion factors) similar energy-level curves are obtained. The main effect of the scaling is to expand the pattern by increasing the crystal-field splittings for any given γ . The scaling has little effect on individual lineshapes, but causes a variation in the overall width of the predicted optical absorption spectra.

4. COMPUTATION OF THE LINESHAPES

The contribution $S_J(\epsilon)$ of the J th transition to the lineshape function is given by

$$S_J(\epsilon) = \int W(\gamma) f_J(|\epsilon_J(\gamma) - \epsilon|) d\gamma, \quad (3)$$

where $W(\gamma)$ is the Boltzmann factor discussed in an earlier section, $\epsilon_J(\gamma)$ is the computed transition energy, and $f_J(|\epsilon_J(\gamma) - \epsilon|)$ is an intrinsic lineshape function. In this formula, it is assumed that the transition moment does not vary with configuration coordinate. The intrinsic lineshape function f_J simulates the effects of all strains other than the twisting distortion. For purpose of computation, f_J is taken to be gaussian,

$$f_J = \exp[-\alpha_J(|\epsilon_J(\gamma) - \epsilon|^2)]. \quad (4)$$

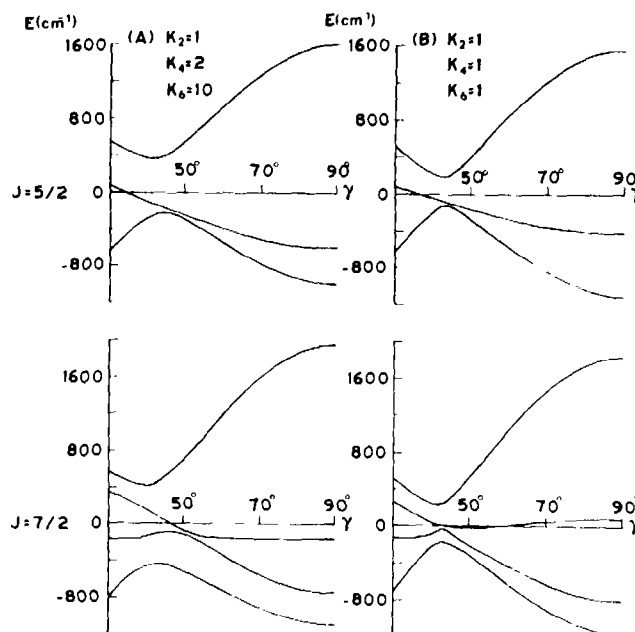


Fig. 6. Crystal-field levels of Yb^{III} as a function of the twist angle γ . The second, fourth, and sixth order crystal-field parameters are scaled by k_2 , k_4 and k_6 respectively. The gaps between the second and third levels of the $J = 5/2$ manifold and between the first and second levels of the $J = 7/2$ manifold indicate the effect of orthorhombic distortion. The values of k_2 , k_4 and k_6 have been computed for this case.

The widths employed were chosen to be as large as possible, compatible with the observed features of each line, in order to minimize irregularities in the lineshape imposed by the finite numerical integration mesh.

The computation of the lineshapes is accomplished through a series of steps. The optical transition energy $\epsilon(\gamma)$, the electrostatic energy E , and the corresponding Boltzmann factor W are calculated as functions of γ in half degree increments. The lineshape functions $S_j(\epsilon)$ are then determined by numerical integration. All $S_j(\epsilon)$ are normalized to equal areas, and the total lineshape function $S(\epsilon)$ is obtained by summing the components with each component weighted by a factor M_j adjusted to reproduce the observed relative intensities.

evaluating the electrostatic energy. The computed electrostatic energy curve has been utilized, but the equilibrium has been arbitrarily shifted to optimize the resulting lineshape. For the case we have been considering (Yb-P distance of 2.6 Å and charge distribution corresponding to a 50 per cent ionicity of the P-O bond) optimum agreement between the computed and observed lineshapes is obtained for an equilibrium value of γ equal to 38°.

If the electrostatic energy curve of Fig. 5 is utilized with equilibrium shifted to 38°, then a small contribution to the lineshape is obtained

from sites with γ less than 30° . On the other hand, it has been shown in a previous section that an effective radius of $1.28 \text{ \AA}$ for the non-bridging oxygens and a $1.0 \text{ \AA}$ radius for Yb^{3+} leads to a Yb-P distance of $2.8 \text{ \AA}$ and a hard sphere contact value of $\gamma = 30^\circ$. To simulate this hard sphere cutoff, an infinite step has been introduced in the electrostatic energy at $\gamma = 30^\circ$. The resulting calculated lineshapes are shown in Fig. 7, and the corresponding values of the parameters α_j and M_j are given in Table 2. It is seen that one narrow line and two broad lines appear in the absorption in agreement with the observed spectrum. In addition, the shapes of the two broad lines are duplicated reasonably well. The skewness of the narrow line, however, is not predicted. The calculated emission lineshape has similar features to the observed spectrum, although detailed agreement is not obtained. Since the highest energy emission line is strongly self-absorbed, this line is somewhat distorted and its relative intensity cannot be inferred from the measured spectrum. Duplication of this line in the computed emission, therefore, is not expected.

5. DISCUSSION

The analysis of the preceding sections shows that the proposed rare earth site model predicts many of the observed features of the Yb^{3+} spectra. While a number of approximations are involved, the final parameter values appear reasonable. Furthermore, the computed lineshapes are insensitive to variations in all parameters except the equilibrium

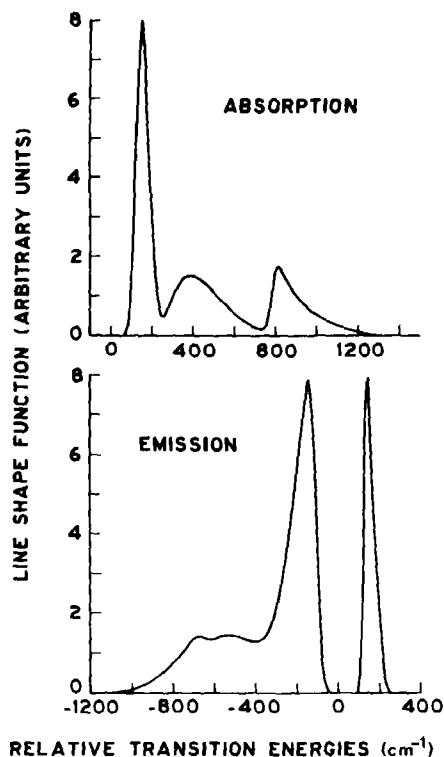


Fig. 7. Calculated lineshapes of Yb^{3+} spectra for twisting distortion of the complex. The Yb-P distance is $2.6 \text{ \AA}$ and a P-O bond ionicity of 50 per cent is assumed.

twist angle γ_0 . In the case used for illustration, the Yb-P distance of $2.6 \text{ \AA}$ compares reasonably with the $2.8 \text{ \AA}$ value deduced from ionic radii, and the 50 per cent ionicity of the P-O bond is within the expected range. Variations of the scale factors k_2 , k_4 and k_6 have been shown to have minor effects on the

Table 2. Gaussian width parameters α_j and intensity factors M_j for the computed spectra. The component lines are numbered in order of increasing relative energy

	Absorption			Emission			
J	1	2	3	1	2	3	4
α_j	0.0025	0.0010	0.0010	0.0005	0.0005	0.0010	0.0025
M_j	1.00	0.69	0.49	0.40	2.00	4.25	1.70

crystal-field levels, and it has been found that the chief effect of increasing the ionic character of the P—O bond or of decreasing the Yb—P distance is to expand the spectrum while preserving individual lineshapes.

To test the sensitivity of the lineshapes to the Boltzmann distribution, a set of absorption and emission spectra have been computed for the optimum parameters using a temperature of 650°K in the Boltzmann factor. Lineshapes comparable to those of Fig. 7 are obtained. Since such a change in temperature is equivalent in effect to an increase in the stiffness of the twisting distortion, this result emphasizes the fact that the computed shapes are not dependent on the sampling of a large number of highly distorted sites. Rather, the widths and skewness of the computed lines are to a large extent determined by the first and second derivatives of the transition energies with respect to γ in the vicinity of the equilibrium. Thus, from Fig. 6, it can be seen that the narrowness of the lowest energy absorption line results from the fact that the lowest crystal-field levels split from the $J = 7/2$ and $J = 5/2$ manifolds track one another rather faithfully over the entire range of configuration coordinate. On the other hand, the second and third levels split from the $J = 5/2$ manifold do not track the lowest lying level of the $J = 7/2$ manifold. The derivatives of the transition energy with respect to γ are large in the vicinity of 38°, and broad lines result. Similarly, the skewness of the second and third absorption lines to higher energies can be attributed to the behavior of the second derivatives of the transition energies with respect to configuration coordinate.

That satisfactory lineshapes can be obtained for various parameter sets is a result of the fact that the general features of the crystal-field-split energy level curves are preserved for a wide range of parameters. As can be seen from Fig. 6, this result holds for the scaling factors which have been applied to the crystal-field parameters as well as to the size and charge factors discussed above. These con-

siderations suggest that the essential features are characteristic of the distortion, and do not depend on a fortuitous specification of a large set of adjustable parameters.

An energy-level diagram derived from the positions of the peaks of the computed absorption and emission spectra is shown in Fig. 8. Comparison with Fig. 3 shows that the splittings of the two 1^6 manifolds deduced from the calculated spectra are somewhat larger than the observed splittings. Since the overall splittings of the $J = 7/2$ and $J = 5/2$ levels are in accord with the observed spectra, this result suggests that the trigonal components of the crystal field are overemphasized in the model.

A possible source of the overemphasis of trigonal fields is our use of tetrahedral bond lengths appropriate to undistorted tetrahedra. Certainly any distortion of the tetrahedral ligands which permits the non-bridging oxygens to assume an arrangement more nearly resembling an octahedron about the rare earth would have the effect of reducing the relative contribution of the trigonal fields. However, while calculations for a complex with in-

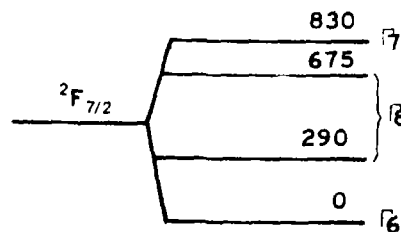


Fig. 8. Energy-level diagram derived from the computed spectra. The levels are labeled according to the octahedral manifolds from which they are derived. The splittings are given in cm⁻¹.

creased phosphorus to non-bridging oxygen bond lengths do show reduced splitting of the Γ_8 levels, an overall decrease of the splitting of the J -manifolds also results.

Finally, with regard to the discrepancy between the required equilibrium value of γ and that derived from the electrostatic energy of the complex, it is noted that the free energy of the entire system must be minimized in order to determine the equilibrium properly. Presumably, our results indicate the importance of energy and entropy terms related to the coupling of the complex to the glass network, and thus limit the extent to which the complex may be considered as an isolated entity.

Acknowledgements—The authors acknowledge discussion of the experimental data with Dr. Charles Robinson and express their thanks to Professor D. R. Uhlmann for several stimulating discussions during the course of the investigation.

REFERENCES

- 1 ROBINSON C. C. and FOURNIER J. I., *Chem. Phys. Lett.* **3**, 517 (1969).
- 2 ROBINSON C. C. and FOURNIER J. I., *J. Phys. Chem. Solids* **31**, 895 (1970).
- 3 BISCOE J., PINCUS A. G., SMITH C. S. and WARREN B. F., *J. Am. ceram. Soc.* **24**, 116 (1941).
- 4 PAULING L., *The Nature of The Chemical Bond*, 3rd Edn, chap. 3, Cornell University Press, New York (1960). GORDY W., *Disc. Faraday Soc.* **19**, 14 (1955). VAN WAZER J. R., *Phosphorous and Its Compounds*, p. 56, Interscience Publishers, New York (1958).
- 5 For discussion of the crystal field theory with particular reference to rare earth ions see JUDD B. R., *Operator Techniques in Atomic Spectroscopy*, Chap. 2, McGraw-Hill, New York (1963); WYBOURNE B. G., *Spectroscopic Properties of Rare Earths*, Chap. 6, Interscience, New York (1965).
- 6 STEVENS K. W. H., *Proc. phys. Soc.* **65A**, 209 (1952); JUDD B. R., *Proc. R. Soc.* **A227**, 552 (1955); FLEISCH R. J. and STEVENS K. W. H., *Proc. R. Soc.* **A219**, 387 (1953); see also LOW W., *Paramagnetic Resonance in Solids*, Suppl. 2 of *Solid State Physics* (Edited by F. Seitz and D. Turnbull), Academic Press, New York (1960).
- 7 FRIEFMAN A. J. and WATSON R. E., *Phys. Rev.* **134**, A1492 (1964).
- 8 AXE J. D. and BURNS G., *Phys. Rev.* **152**, 331 (1966); WATSON R. E. and FRIEFMAN A. J., *Phys. Rev.* **156**, 251 (1967); FLEIS M. M. and NEWMAN D. J., *J. chem. Phys.* **47**, 1986 (1967); BISHOP S. S., FLEIS M. M., NEWMAN D. J. and SMITH J., *J. chem. Phys.* **47**, 4133 (1967); FLEIS M. M. and NEWMAN D. J., *J. chem. Phys.* **49**, 4037 (1968).
- 9 BURNS G., *Phys. Rev.* **128**, 2121 (1962); FENNANDER R. C. J. and WONG F. Y., *J. chem. Phys.* **38**, 2750 (1962); RAY D. K., *Proc. Phys. Soc. Lond.* **82**, 47 (1963); WATSON R. E. and FRIEFMAN A. J., *Phys. Rev.* **133**, A1571 (1964).
- 10 HUTCHINGS M. F. and RAY D. K., *Proc. Phys. Soc. Lond.* **81**, 663 (1963); BLANEY B., *Proc. R. Soc.* **277**, 289 (1964).
- 11 BURNS G. and AXE J. D., *Optical Properties of Ions in Solids* (Edited by H. M. Crosswhite and H. W. Moos) p. 53, Interscience, New York (1967).
- 12 POWELL M. J. D. and ORBACH R., *Proc. Phys. Soc. Lond.* **78**, 753 (1961).
- 13 BRADBURY M. I. and NEWMAN D. J., *Chem. Phys. Lett.* **1**, 44 (1967).

ELECTRON MOBILITIES AND PHOTOLUMINESCENCE OF SOLUTION GROWN INDIUMPHOSPHIDE SINGLE CRYSTALS

O. RÖDER, U. HEIM and M. H. PILKUHNS

Physikalisches Institut, Universität Frankfurt/M., Germany

(Received 8 December 1969; in revised form 9 February 1970)

Abstract—InP single crystals were grown from an indium solution. They show a typical dendrite structure. The electron concentration ranges from 10^{16} to 10^{19} cm⁻³. The dependence of the room temperature Hall mobility on the electron concentration is compared with the theoretical curves of Moore and Brooks-Herring. Photoluminescence spectra of relatively pure undoped samples show two major emission bands at low temperatures, one near 1.416 eV (containing four emission lines) and a band near 1.38 eV. Time resolved spectroscopy shows that the 1.38 eV band is due to donor-acceptor pair recombination. At high doping levels the luminescence spectra show a pronounced Burstein-Moss shift to higher energies, the band-acceptor transition gains in relative intensity and broadens considerably. Above 10^{18} cm⁻³ it is the only remaining emission band at low temperatures. The shift of the Fermi level with carrier concentration is compared with the theory assuming a parabolic conduction band. It is found, that the experimental shift does not follow quantitatively the expected Burstein-Moss shift, presumably due to band tailing and gap shrinkage effects.

1. INTRODUCTION

INP HAS A DIRECT bandgap of 1.42 eV at low temperature, i.e. only 0.1 eV below that of GaAs. The effective electron mass is presumably of similar magnitude for both materials, namely about $0.07 m_0$ [1]. In contrast to GaAs not much information has been reported either on crystal growth, mobilities or on luminescent properties of InP. Turner *et al.* [2] and Leite [3] investigated the optical absorption and emission of not intentionally doped InP in the electron concentration range from 9×10^{15} to 4×10^{17} cm⁻³. Their spectra show a near edge emission at about 1.416 eV and a second emission band near 1.36 eV [2] or 1.38 eV [3]. The 1.416 eV emission has been ascribed to the free exciton decay [2] and the 1.38 eV emission to a donor-acceptor transition [3]. Recently, Heim [4, 27] demonstrated by time resolved spectroscopy that the 1.38 eV emission can be indeed described by a donor-acceptor pair mechanism. The intensity dependence on excitation intensity of several emission lines near the fundamental gap between 1.40 and 1.42 eV was investigated by

Heim *et al.* [5, 27]. No photoluminescence data have been published till now for highly doped InP.

A reason, why InP is much less investigated than GaAs, is not clear.

In this paper the photoluminescence of InP crystals was investigated, in particular its dependence on doping level, temperature and excitation intensity.

2. EXPERIMENTAL

2.1. Preparation of crystals

InP melts at 1065°C under a phosphorus dissociation pressure of more than 15 atm. [8]. In our experiments the high phosphorus pressure was avoided by using a solution growth method first reported by Wolff *et al.* [9]. Polycrystalline InP (purchased by Monsanto

or Minig and Chemical Products) was re-grown from a dilute In-InP solution. This method has the advantage of a relatively low growth temperature and therefore the possibility of contaminating the crystals by the container material is decreased. Many of the impurities introduced with the InP charge are diluted or extracted by the large excess of the indium solvent. *N*- and *p*-type doping was achieved by addition of metallic tellurium or zinc to the solution. The In-InP mixture was placed into a cleaned and vacuum heated quartz container tube of about 100 cm³ volume, which was then evacuated to 5×10^{-5} Torr and sealed. A typical charge was 6 g In and 1 g InP corresponding to a phosphorus content of 10 at %. The sealed tube was supported in a vertical tube furnace (length 1 m, ϕ 30 mm) at a temperature 40–50°C above the saturation solubility temperature for some hours to ensure complete solution of the InP. It was then lowered through the built-in temperature gradient at an average cooling rate of 10°C/h. The excess indium was dissolved in cold conc. HNO₃.

2.2. Measurement techniques

The samples were characterized by Hall- and resistivity measurements. Contacts were provided by alloying tin into *n*- and indium-zinc into *p*-material. The *n*-contacts had a series resistance of a few ohms. Major difficulties were encountered making ohmic contacts to *p*-material.

The luminescence was measured by a conventional apparatus involving a lock-in amplifier technique. We used an immersion Dewar vessel, a 30 mW He-Ne-laser for illumination and a Spex-1700-III-grating spectrometer with a resolution of better than 0.2 meV whenever necessary. The excitation intensity was varied by insertion of neutral density filters. The spectrograph was calibrated by means of the laser lines. The signal was detected by a cooled photomultiplier with S1-characteristic. The experimental setup for the time resolved measurements was described

earlier[4]. Careful etching of the crystal surface was found to be necessary in order to eliminate erroneous luminescence bands, which are caused by surface effects.

3. RESULTS AND DISCUSSION

3.1. Crystal morphology

Solution grown InP single crystals show the characteristic dendrite structure typical for almost all crystals of elemental and compound semiconductors grown from a metallic solution. A great diversity of these dendrites was found. In Fig. 1(a), (b) and (c) typical dendrites which are frequently observed are exemplified. The common characteristic of all the crystals investigated is the twinned structure, with twinning taking place invariably between the flat (1, 1, 1) and $(\bar{1}, \bar{1}, \bar{1})$ surfaces of the platelets. An illustration of the twin structure is given in Fig. 1(d). It shows the tip of a dendrite crystal, terminated by {1, 1, 1}-planes. The intersection of two {1, 1, 1}-terminal planes coincides with the twin plane in the crystal. In the case of Fig. 1(d) these twin planes are perpendicular to the plane of view. In general, we obtained nearly the same results as Foster *et al.*[7] reported earlier for solution grown GaP. A more detailed discussion involving the twinning problems in polar semiconductors is found in the review articles by Sangster[10] and Faust and Lindbergh[11].

No difficulties were encountered in doping the crystals *n*- and *p*-type. The largest crystals were obtained for high tellurium doping. The maximum crystal sizes reached were $10 \times 4 \times 2$ mm³.

3.2. Electron mobility

The electron mobility was measured in the doping range (Te-doping) between 10^{16} and 2×10^{19} cm⁻³. Room temperature mobilities are depicted in Fig. 2 as a function of the electron concentration. Samples with a carrier concentration smaller than 10^{17} cm⁻³ are not intentionally doped. The mobility decreases monotonically with increasing carrier concen-



Fig. 3(a). Typical solution grown InP crystals. (b) Flat (1, 1, 1)-In surface of a standard type crystal used for photoluminescence measurements. (c) Facetted long dendrite crystals. (d) Tip of a crystal containing three twin planes

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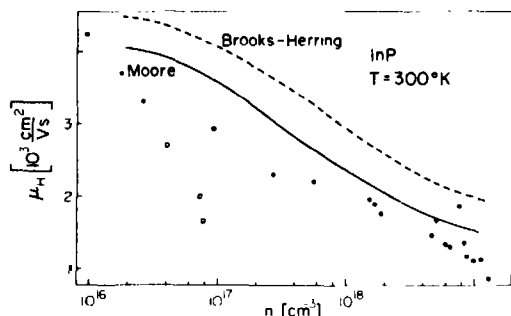


Fig. 2 Room temperature Hall mobility as a function of the electron concentration (Te-dopant). Squares indicate copper contaminated samples. Theoretical values are calculated after Moore[13] and Brooks-Herring[14] using Ehrenreich's[15] mobility limit of $4\,700\text{ cm}^2/\text{Vsec}$.

tration. A qualitatively similar curve has been found in solution grown GaAs[12]. The samples designated by squares in Fig. 2 have usually low mobilities. These samples were contaminated with copper, as revealed by a spectrographic analysis of the indium solvent. These particular samples also exhibit a very strong luminescence band at 1.2 eV (compare Fig. 7 of Section 3.4), which is most likely caused by deep impurity levels due to copper.

We have compared our experimental data with the theoretical dependence of the mobility on donor concentration. The solid line in Fig. 2 refers to Moore's theory[13], the dotted line to the Brooks-Herring formula[14]. Ehrenreich's[15] room temperature value of $4\,700\text{ cm}^2/\text{Vsec}$ for the mobility limit due to polar lattice scattering was assumed. Lattice scattering was combined with ionized impurity scattering by summation of reciprocal mobilities. For the electron effective mass and for the dielectric constant the same values as for GaAs were used ($m_n = 0.07 m_0$ [1] and $k = 13.5$ [16]). Good agreement between experimental data and Moore's theory is found in the high doping range. Experimental mobilities are somewhat lower than predicted in the concentration range between 10^{16} and 10^{18} cm^{-3} . Since Moore's treatment is confined to degenerate material, this disagreement is not surprising. The Brooks-Herring expression

with Ehrenreich's mobility limit does not fit our experimental data. Recently Hilsum and co-workers[17] published electron mobility data of InP crystals with a low electron concentration. From their data as well as from their theoretical considerations a mobility limit higher than Ehrenreich's value results, namely $5\,800\text{ cm}^2/\text{Vsec}$. So far, we have not sufficient experimental data in the low concentration range to decide, which mobility limit is correct.

3.3. The Luminescence at low electron concentrations and low temperatures

The luminescence data in this section refer to not intentionally doped crystals and to the temperature range between 1.8 and 20°K . Different samples with electron concentrations between $9 \times 10^{15}\text{ cm}^{-3}$ and $1 \times 10^{17}\text{ cm}^{-3}$ were used. A spectrum typical for low electron concentration is shown in Fig. 3. It contains a band *A* at 1.416 eV , which is the unresolved near edge emission. Its fine structure depends on the illumination intensity and will be discussed below in more detail. Furthermore, a band *B* at about 1.375 eV is observed; which can be attributed to a donor-acceptor pair

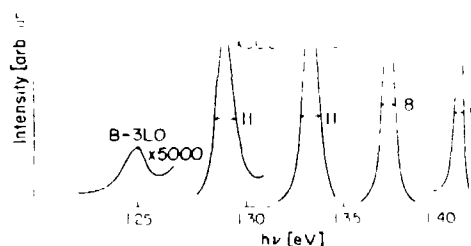


Fig. 3 Typical photoluminescence spectrum of a not intentionally doped sample at 1.8 K . Line *A* is unresolved donor valence band/exciton recombination, line *B* a donor-acceptor pair recombination with three phonon satellites. The linewidths are given in meV.

Phonon cooperation. We observe three additional lines, designated as B-LO, B-2LO and B-3LO in Fig. 3. These lines are apparently phonon satellites of the pair recombination line *B*. The phonon replicas yield a phonon energy of (42.5 ± 0.5) meV as an average value derived from data of 8 samples. This result agrees well with the corresponding infrared reflectivity (43 meV, 28, 18) and Raman data (42.8 meV, 17). In Table 1, data concerning the phonon cooperation are listed for InP and GaAs[20] samples containing acceptors with different binding energies E_a . The donor binding energy is assumed to be constant and small (< 8 meV). From Table 1 it can be seen that larger values of E_a are associated with stronger phonon cooperation. No significant change of the intensity ratio I_B/I_{B-LO} with temperature has been found for InP in the range between 1.8 and 20°K.

Table 1. Intensity ratios of line *B* (peak energy E_B) and its first phonon satellite (line B-LO) for three different acceptor binding energies E_a ($E_a = E_{\text{acceptor}} - E_D \approx 8$ meV) in InP and GaAs[20].

InP			
E_a	32	37	48
meV	(Ref. [3])	(this work)	(Ref. [2])
I_B/I_{B-LO}	15.23	15.20	4.5
GaAs			
E_a	19.5	28	35
meV			
I_B/I_{B-LO}	48	33	22

We have compared our results with theoretical data derived from Hopfield's 'shallow trap model'[21] which, however, is confined to trap energies larger than the LO-phonon energy. Experimentally we find the following intensity ratios for subsequent phonon replicas, 1:0.055:0.0027:0.0001. The theoretical coupling factor turns out to be much too large (by about two orders of magnitude), and a Poisson distribution would lead to a somewhat more rapid decrease of the intensity of subsequent phonon satellites.

The donor-acceptor recombination band *B*. As was confirmed recently by time resolved spectroscopy[4, 27], band *B* should be assigned to a donor-acceptor pair transition. A peak shift to lower energies and a steepening of the high energy shoulder of the band were observed for spectra at increasing times after excitation. The time decay of the integrated emission of band *B* could be described using a decay model of Thomas *et al.*[22]. The fit of the theoretical curves to the experimental data yielded an effective Bohr-radius of 90–100 Å for the donor and a transition probability $W_{\text{max}} = 7 \times 10^7 \text{ sec}^{-1}$. Qualitatively similar results have been reported for the case of GaAs[19].

Figure 4 demonstrates the influence of excitation intensity on band *B*, when excited with the d.c. He-Ne-laser (maximum photon

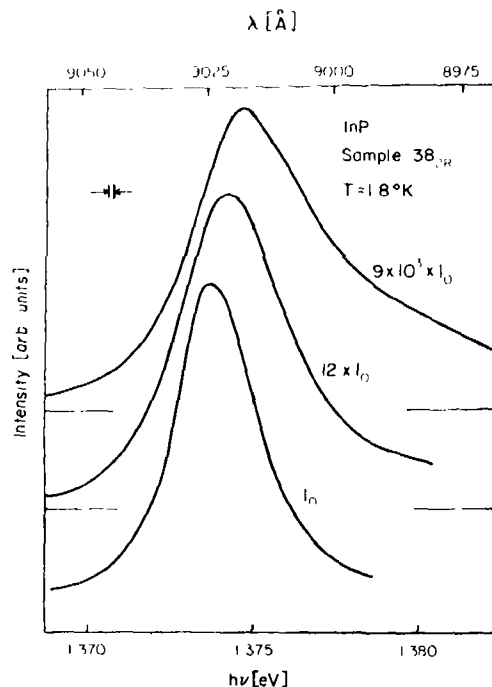


Fig. 4. Emission in band *B* (sample 38_R, $n = 9.7 \times 10^{15} \text{ cm}^{-3}$) at 1.8°K for three different excitation levels. The lowest excitation intensity I_0 corresponds to $10^{17} \text{ photons/cm}^2 \text{ sec}$.

flux 10^{21} photons/cm². sec). The sample 38_{2R} used for this measurement has a carrier concentration of $n = 9.7 \times 10^{15}$ cm⁻³. As may be seen from Fig. 4, band *B* shifts slightly to higher energies and broadens on the high energy side, when the excitation intensity is increased. Very similar behaviour was reported recently for a pair band in weakly doped GaAs[23].

The near edge emission band A. At high resolution the emission band *A* was found to consist of several narrow lines when weakly doped samples and low excitation levels were used. In Table 2 peak energies, linewidths and tentative assignment of the lines are given. The influence of excitation intensity and the nature of these emission lines have been briefly discussed in preceeding communications[5, 27]. The discrepancy between earlier published data for the energetic position of the near edge emission (1.4165 eV Turner *et al.* [2], 1.413 eV Leite[3]) can now be explained as resulting from different excitation levels in the experiments.

egrated emission in band *A* increases linearly in the whole range of the He-Ne-laser excitation.

The spectra at elevated temperatures show a different behaviour (Fig. 5(b)). The narrow line at 1.4143 eV, which was ascribed to a bound exciton[5] vanishes at temperatures above 14°K. Contrary to the intensity effect, the 1.4165 eV line remains the dominant line in the whole temperature range considered. It shifts only slightly to lower energies as the temperature is raised. The results of Fig. 5(b) are consistent with the interpretation of the 1.4143 eV line as a bound exciton line and the 1.4165 eV line as the free exciton line. The difference of the two energies, i.e. 2.2 meV, is the binding energy of the exciton to the localized center. When the temperature is raised, we would indeed expect, that less excitons are bound to this center.

The assignments of the excitation lines (Table 2) are not unambiguous in view of the following discussion of the 1.418 eV shoulder on the high energy side of band *A*: It may be

Table 2. Peak energies and halfwidths of weakly doped samples at
Accuracy of the peaks

Peak energy eV	Halfwidth meV	
1.418	shoulder	
1.4165	0.8	
1.4143	0.6	bound exciton
1.4126	1.5	donor
1.375-1.385	3-8	donor-acceptor pair transition

In Fig. 5(a) and 5(b) the effects of excitation intensity at constant temperature and of temperature at constant excitation intensity are compared. More photons are emitted in the lower energy lines, when the excitation intensity is increased at constant temperature [5] (Fig. 5(a)). We have also studied the intensity of the isolated 1.4165 eV line as a function of the excitation level and found, that it saturates at high excitation intensities. On the other hand it was observed, that the in-

noticed in Fig. 5(b) that this shoulder increases in relative intensity as the temperature is raised. Assuming a value of 1.4205 eV for the bandgap[2], this shoulder cannot be interpreted as a hydrogenic excited state of a free exciton at 1.4165 eV. Possibly the shoulder might be due to the free exciton itself.

A comparison of the curves in Fig. 5(a) and 5(b), which exhibit quite different behaviour, leads to the conclusion, that sample heating and excitation level influence the spectra in a

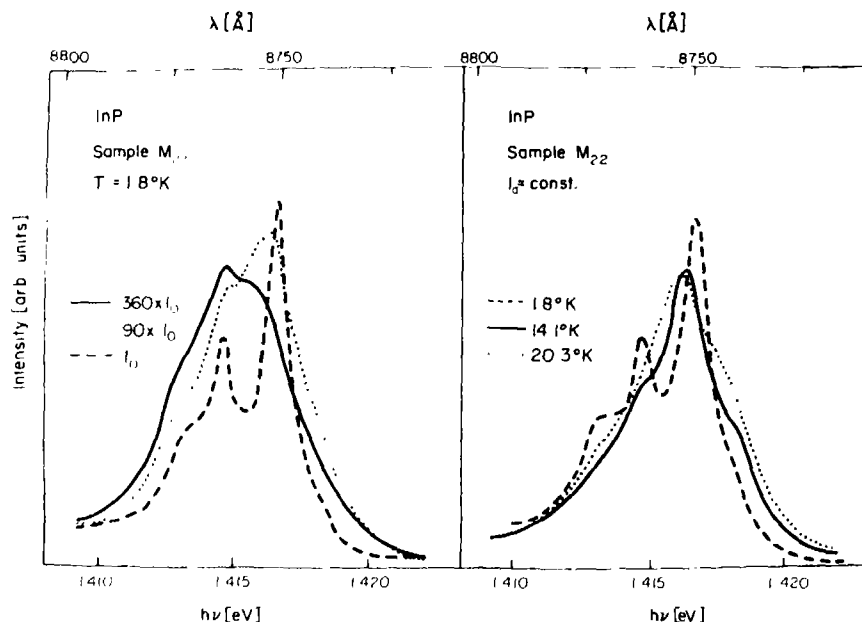


Fig. 5. Photoluminescence spectra (band A) of InP ($n = 9.7 \times 10^{15} \text{ cm}^{-3}$) (a) at 18°K for three different excitation levels (He-Ne laser). The lowest excitation intensity I_0 corresponds to 3×10^{18} photons/cm² sec. (b) At constant excitation level for three different temperatures. Different arbitrary intensity scales have been used.

different manner. This means in particular, that a genuine effect of excitation level is present besides sample heating. In Fig. 6 the emission for the case of very high excitation intensities (N_2 -pulse laser) is shown. Besides band A a new emission line emerges at about 1.407 eV, which dominates the spectrum at highest excitation levels. This line narrows and shifts continuously to lower energy when the excitation intensity is increased. The luminescence intensity of this new line increases stronger than quadratically with excitation intensity. At highest excitation levels the decay time of this line shortens beyond our resolution limit of about 3 nsec. These observations are interpreted in terms of many-body interaction effects and stimulated emission[5].

3.4. Temperature dependence of the luminescence

Luminescence spectra at three different

temperatures are shown in Fig. 7 for a sample with a donor density of $2 \times 10^{17} \text{ cm}^{-3}$ and in addition containing deep impurity levels. The spectrum at 4°K shows line A and B together with phonon satellites and a deep impurity line C, which is discussed in detail below.

As the temperature is raised, the line structure of the near edge emission line A first changes and finally disappears completely. The temperature dependence of this line structure has already been discussed in Section 3.3. At 77°K band A contains no detectable substructure and it should be now interpreted as band-to-band recombination[3]. Line B has been interpreted as donor-acceptor-pair transition at the lowest temperature. At elevated temperatures it should become the conduction band-acceptor transition, as was recently investigated for Ge-Ge-pairs in GaAs[23]. Phonon satellites have not been detected above 77°K.

Notice that line A is weaker in intensity than

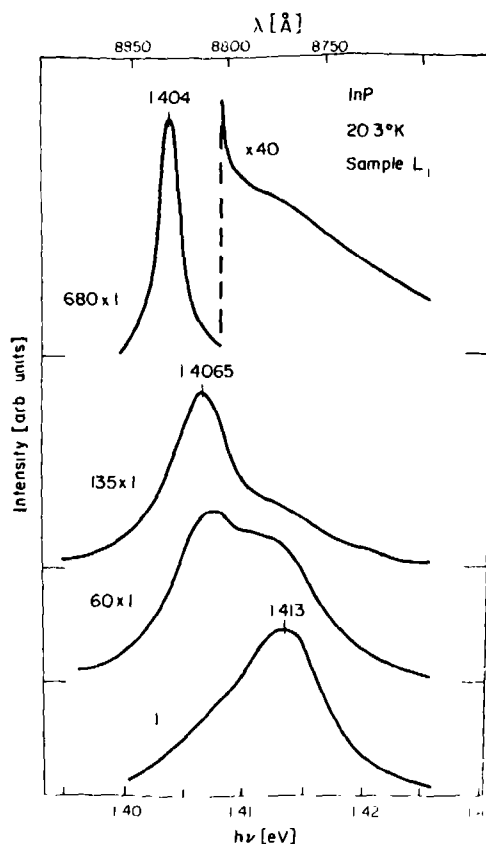


Fig. 6 Photoluminescence spectra of InP ($n = 9.5 \times 10^{17} \text{ cm}^{-3}$) at 20°K for several excitation levels with the λ pulse laser. The lowest excitation intensity I corresponds to $2 \times 10^{22} \text{ photons/cm}^2 \cdot \text{sec}$.

line *B* by a factor of about 40 at 4°K. At 77°K, line *A* dominates and exceeds the intensity of line *B* by a factor of 4. At room temperature only one considerably broadened emission band is observed, which is presumably the band-to-band transition. This effect of temperature on the relative intensities of line *A* and *B* may be explained in the following way: at higher temperatures it will become more difficult to trap a hole at an acceptor level, hence the band-to-band transition will prevail. Line *A* shifts to lower energies as the temperature is raised. This shift coincides with the energy gap variation as reported by Turner[2].

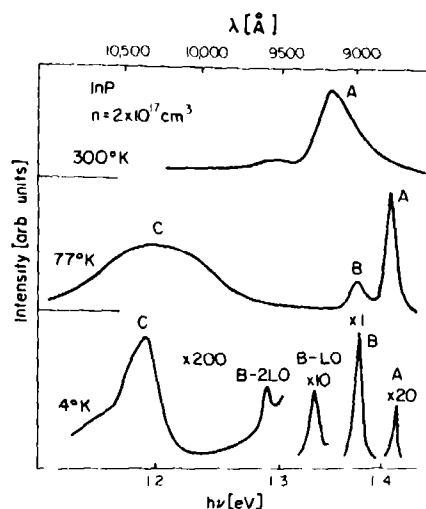


Fig. 7 The emission spectrum for three different temperatures, $n = 2 \times 10^{17} \text{ cm}^{-3}$.

At low energy an additional emission line is observed near 1.2 eV in the sample of Fig. 7. This emission line was particularly intense in samples, which were contaminated with copper. We therefore attribute the 1.2 eV line to a

the luminescence spectra at 77°K is demonstrated in Fig. 8. At the lowest doping level, one can clearly distinguish between the band to band transition line *A*, the band to acceptor recombination line *B* and a phonon satellite to line *B* as described above for undoped samples. Since these data refer to 77°K, line *A* is the band to band transition and line *B* the conduction band to acceptor transition. As the doping level increases, the relative intensity of the impurity band *B* increases strongly in comparison with that of line *A*. Simultaneously both bands broaden considerably. In the doping range above 10^{18} cm^{-3} both bands shift to

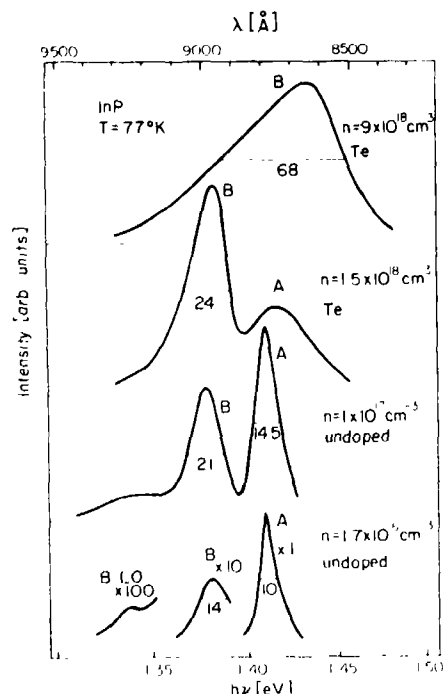


Fig. 8. Photoluminescence spectra for various doping levels at 77°K. Intensities are plotted in arbitrary linear scale. Line *A* is the band to band transition, line *B* the conduction band/donor to acceptor recombination line. The linewidths are given in meV.

higher energy. The relative intensity of the phonon satellites to line *B* decreases as the doping level is raised. Above 10^{18} cm^{-3} phonon satellites are no longer detectable. At the highest doping level line *A* disappears completely and the remaining line *B* broadens and shifts to still higher energies. It may be noticed, that the line is strongly asymmetrical and has a pronounced low energy tail (upper curve).

Figure 9 displays the peak energies of line *A* and *B* as a function of carrier concentration at 20°K. One can clearly see, that the peak energy of line *A* remains approximately constant. As shown before in Fig. 8, its intensity decreases considerably with increasing carrier concentration. Line *A* could not be detected at concentrations higher than $2 \times 10^{18} \text{ cm}^{-3}$. The peak energy of line *B* begins to rise very

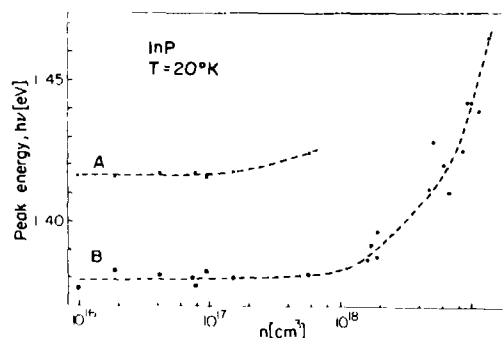


Fig. 9. Concentration dependence of the peak energy of lines *A* and *B*. Samples with an electron concentration below 10^{17} cm^{-3} are undoped, others tellurium doped.

rapidly above 10^{18} cm^{-3} , just in that range, where line *A* disappears. In our interpretation, the disappearance of line *A* at high donor concentrations implies a preference for hole recombination via acceptors instead of direct recombination with electrons. A reasonable interpretation is an increase in the number of compensating acceptors, possibly silicon from the quartz crucible. The peak shift of line *A* and *B* to higher energy can be interpreted as the familiar Burstein-Moss shift, i.e. a filling of the conduction band with electrons.

We have tried to deduce the shift of the Fermi-level from the luminescence spectra at 20°K as a function of carrier concentration. The high energy cut-off ($I(E_{\text{cut-off}}) = 0.1 \times I_{\text{peak}}$) of the luminescence band can be assumed to be a reasonable measure for the position of the Fermi-level. The experimental shift of the Fermi-level was found to be smaller by a factor of about two than the theoretically expected one, computed on the basis of a constant effective mass ($m = 0.07 m_0$). The following reasons may be found to explain this behaviour: at high donor concentrations a gap shrinkage with the formation of tail states takes place, reducing the full band filling effect. Simultaneously the acceptor level broadens to an impurity band leading to the same effect. The effective electron mass increases due to nonparabolicity when the

Fermi-level moves up in the conduction band as reported earlier for GaAs[24].

Which of the three effects prevails, is not clear, however, they all reduce the expected Burstein-Moss shift. An illustration of the broadening of the emission line *B* as a function of electron concentration is given in Fig. 10. (Halfwidths are plotted vs. electron concentration in double logarithmic scale). The solid line inserted for comparison represents a $\Delta E = n^{1/3}$ relation. At the highest doping levels the experimental points are above this line. The line broadening is a typical high concentration effect which can be attributed to the conduction band tails and a broadening of the acceptor states. The same $\frac{1}{3}$ -slope as in Fig. 10 was found for the increase of the linewidth with donor density in the cathodoluminescence of GaAs[25].

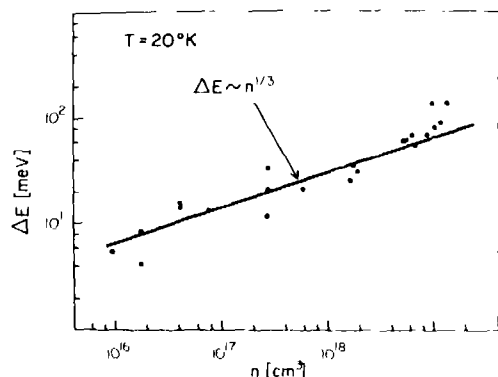


Fig. 10. Dependence of the emission linewidth on electron concentration at 20°K (double logarithmic scale).

3.6. Luminescence of p-type InP

Zinc-doped InP crystals were grown in the high doping range only. The luminescence of these samples at 77°K is depicted in Fig. 11. At the lowest acceptor concentration of $1.4 \times 10^{18} \text{ cm}^{-3}$ the peak energy lies at 1.366 eV, which falls below the peak energy of line *B* in *n*-type samples.

As in GaAs[26] the emission peak shifts to lower energy with increasing acceptor concentration and the lines broaden considerably.

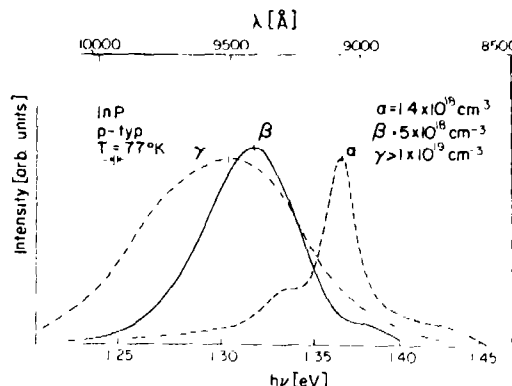


Fig. 11. Spectra of three p-type samples at various doping levels.

The shift to lower energies is usually attributed to a 'gap shrinkage' effect. Although we see some structure on the high energy side of the main emission band, it is not clear, whether a band filling effect is present, as reported by Cusano[26] for GaAs. In summary the general appearance of the luminescence of p-type InP is very similar to that of p-GaAs.

Acknowledgements

1. BALKANSKI M. and AMZALLAG E. (to be published article) *Phys. Status Solidi*, **30**, 407 (1968).
2. TURNER W. J. and PELLER G. D. *Appl. Phys. Lett.*, **3**, 102 (1963).
3. TURNER W. J., REESE W. F. and PELLER G. D. *Phys. Rev.*, **136**, A1467 (1964).
4. FETTER C. C. *Phys. Rev.*, **157**, 672 (1967).
5. HEIM U. *Solid State Commun.*, **7**, 445 (1969).
6. HEIM U., RÖDER O. and PIHKUN M. H. *Solid State Commun.*, **7**, 1173 (1969).
7. MULLIN J. B., HERITAGE R. T., HOLLIDAY C. H. and STRAUGHAN B. W. J. *Crist. Growth*, **3**, 281 (1968).
8. FOSTER T. M., PLASKETT T. S. and SCARDEFIELD J. F. *IBM J. Res. Dev.*, **10**, 114 (1966).
9. v. d. BOOMGAARDT and SCHOLK. *Philips Res. Rep.*, **12**, 127 (1957).
10. WOLFE G. A., KECK P. H. and BRODER J. P. *Phys. Rev.*, **94**, 753 (1954).

10. SANGSTER R. C., "Prep. and Prop. of III-V-Compounds", (Edited by R. K. Willardson and H. L. Goering) chap. 28 Reinhold Publishing, New York (1962).
11. LINDBERG O. and FAUST Jr. J. W., *ibid.*, chap. 34.
12. SOLOMON R., *Gallium Arsenide, Proc. of the 2nd Int. Symp.*, p. 11, Dallas (1968).
13. GOODWIN A. R., DOBSON C. D. and FRANKS J., *ibid.*, p. 36.
14. MOORE F. J., *Phys. Rev.* **160**, 618 (1967).
15. BROOKS H., *Adv. Electronics Electron Phys.* **7**, 87 (1955).
16. EHRENREICH H., *J. Phys. Chem. Solids* **12**, 97 (1959).
17. HILSUM C. and ROSE-INNES A. C., *Semiconducting III-V-compounds*, p. 181 Pergamon Press, Oxford (1961).
18. HILSUM C., FRAY S. and SMITH C., *Solid State Commun.* **7**, 1057 (1969).
19. NEWMAN R., *Phys. Rev.* **111**, 1518 (1958).
20. DINGLE R. and RODGERS K. F., *Appl. Phys. Lett.* **14**, 183 (1969).
21. DINGLE R., *Phys. Rev.* **184**, 788 (1969).
22. SCHAIRER W., private communication.
23. HOPFIELD J. J., *J. Phys. Chem. Solids* **10**, 110 (1959).
24. THOMAS D. G., HOPFIELD J. J. and AUGUSTYNIAK W. M., *Phys. Rev.* **140**, A202 (1965).
25. SCHAIRER W. and GRAMANN W., *J. Phys. Chem. Solids* **30**, 2225 (1969).
26. YFE J. H. and CONDAS G. A., *J. appl. Phys.* **39**, 351 (1968).
27. PILIER H., *J. phys. Soc. Japan Suppl.* **21**, 206 (1966).
28. PANKOVE J. I., *J. appl. Phys.* **39**, 5368 (1968).
29. CUSANO D. A., *appl. Phys. Lett.* **7**, 151 (1965).
30. HEIM U., RÖDER O., QUEISSER H. J. and PILKUHNS M. H., *J. Luminesc.* **1**, 608 (1969).
31. KÖHL F., *Infrared Reflectivity of InP*.

PRESSURE AND COMPOSITION DEPENDENCE OF THE ORDER-DISORDER CRITICAL TEMPERATURE OF α -CoFe*

DUK N. YOON† and RONDO N. JEFFERY

Department of Physics and Materials Research Laboratory, University of Illinois, Urbana,
Ill 61801, U.S.A.

(Received 26 November 1969; in revised form 27 January 1970)

Abstract—The pressure dependence of the order-disorder critical temperature T_c of α -CoFe has been measured. The results are used to convert T_c 's measured at various compositions to values corresponding to constant lattice parameter. The resulting composition dependence of T_c is asymmetric about 50:50 composition. This asymmetry implies that any model based on pairwise interactions that are independent of composition is insufficient to describe the transformation over the composition range in which it is observed.

THE VALIDITY of Ising model calculations in describing order-disorder transformations has been the subject of several recent investigations. Measurements of the temperature dependence of neutron diffraction intensity [1] and specific heat [2] near T_c in β -CuZn show good agreement with recent series expansion treatments of the nearest-neighbor Ising model. Other calculations [3, 4] have shown, however, that the inclusion of long range interactions in the Ising model has little effect on the critical indices. Therefore these experimental results are not sufficient to justify the conclusion that only nearest neighbor interactions are important.

Using the same series expansion treatment of the nearest-neighbor Ising model, Bienenstock and Lewis [5] calculated the composition dependence of T_c and obtained results which disagree with experiment for β -CuZn. Hence they conclude that no single pairwise interaction energy, which depends only on the volume, can describe the interaction over the

composition range in which the transition is observed. The same conclusion is reached by Yoon and Bienenstock [6] from the observed pressure dependence of T_c for various compositions in β -CuZn. They suggest that interactions longer than nearest-neighbor play an important role in the order-disorder transition.

where Q_A and Q_B are the number of A and B atoms, respectively, Q_{AB}^j is the number of j -th neighbor A - B pairs, and z^j is the number of j -th neighbors. The energy V^j is given by

$$V^j = V_{AB}^j - \frac{1}{2}(V_{AA}^j + V_{BB}^j),$$

where V_{AA}^j , V_{BB}^j and V_{AB}^j are the interaction energies between j -th neighbor pairs of AA , BB and AB atoms, respectively. The second term in equation (1) is independent of configuration for each composition and does not

*This research was supported in part by the U.S. Atomic Energy Commission under Contract AT(11-1)-1198.

†Present address, Dept. of Chemical Engineering and Materials Sciences, Wayne State University, Detroit, Mich 48202, U.S.A.

contribute to the ordering energy. Therefore, ignoring the second term of equation (1), the partition function may be written as

$$Z = \sum_{c(Q_i)} \exp \left(- \sum_j Q_{AB} V^j / kT \right) \quad (2)$$

where the summation is over only those configurations, $c(Q_i)$, consistent with a fixed composition. Each term in the exponential is invariant under interchange of A and B atoms for each particular configuration. Hence, the partition function is also invariant under interchange of A and B atoms. Since T_c is determined from the partition function, T_c should vary symmetrically with composition about 50:50.

The basic assumption in this model is that the pairwise interaction energies are independent of composition. It is further assumed that the transition occurs at a constant volume, since the interaction energies can be expected to vary with composition due to changes in the lattice parameter. Therefore, in comparing the observed composition dependence of T_c with the predictions of this model, the observed T_c 's have to be converted first to values

the stoichiometric composition (approximately 30 to 75 at.% Co) [8–10]. Hence it is an ideal system to test the composition dependence of T_c predicted by theories.

We measured the pressure dependence of T_c in α -CoFe specimens containing approximately 51, 52, and 52.5 at.% Co over a range of pressure to 7 kbar. The argon gas pressure system and the differential thermal analysis technique used were similar to those of Yoon and Bienenstock [6]. In our measurements, both specimen and 'dummy' were placed in the furnace inside the pressure bomb. The electrical leads were brought out through oil frozen in 'U' shaped high pressure tubings. The DTA signals were sufficient to allow determination of T_c to about $\pm 0.3^\circ\text{C}$ with the temperature increasing. With decreasing temperature, T_c could not be determined so accurately, but appeared to be about 1°C lower than T_c determined with increasing temperature.

Figure 1 shows a typical experimental result of the observed T_c of an α -CoFe specimen to 7 kbar. The data obtained with increasing pressure showed some variation

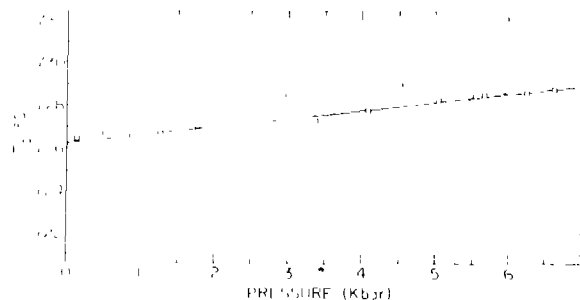


Fig. 1. Observed critical temperature as a function of pressure for an α -CoFe specimen. The circles and squares represent data taken with pressure increasing and decreasing, respectively.

corresponding to constant lattice parameter. Such a correction requires data on the pressure dependence of T_c .

α -CoFe has a CsCl-type structure in the ordered phase and shows the order-disorder transition over a wide range on both sides of

from run to run. This variation appeared to depend on the length of time allowed for the system to reach thermal equilibrium after the admission of cold gas to raise the pressure. In runs when longer times were allowed between raising the pressure and measuring T_c (1–2

hr compared with 10–20 min), the data taken with increasing and decreasing pressure were in much better agreement. On the other hand, in all runs the data taken with decreasing pressure were quite reproducible. Thermal equilibrium between furnace and bomb should be more readily attained on the decreasing pressure cycle since the pressure vessel will already be hot and no cold gas is being added. Therefore, we ignored the increasing pressure data in calculating $\delta T_c/\delta P$. No systematic composition dependence of $\delta T_c/\delta P$ could be observed among the three samples used in our experiments. From ten separate measurements on these samples, the average value of $\delta T_c/\delta P$ we obtain is $0.40 \pm 0.09^\circ\text{C/kbar}$. The error indicates root-mean-square deviation from the average. Recent data of Getting and Kennedy[11] show that the pressure correction for Chromel–Alumel thermocouples is negligible for the pressure and temperature range used in our experiment.

Conversion from the observed $\delta T_c/\delta P$ to $\delta T_c/\delta a$, where a is the lattice constant, requires knowledge of the compressibility K at T_c . This was estimated from Bridgman's compression measurements for α -CoFe– α -Fe[12], recent elastic constants measurements on α -Fe[13], and the measured temperature dependence of the elastic constants of α -Fe[14] and β -CuZn[15]. The estimated value of K for 50:50 α -CoFe near T_c is $7.8 \times 10^{-4}/\text{kbar}$. This gives a value of $\delta \ln T_c/\delta \ln a = -1.5$ from the observed value of $\delta T_c/\delta P$.

Assuming now that $\delta \ln T_c/\delta \ln a$ is the same at all compositions in the α -CoFe range, the observed[10] T_c at each composition was corrected to the value corresponding to the lattice constant of 50:50 α -CoFe at its T_c . For this correction, we used the results of Asano *et al.*, on the room temperature lattice constants at various compositions[10]. Their data show that the lattice constant of α -CoFe decreases with Co content by approximately 0.5 per cent between 40 and 60 at.% Co. In addition, we took into account

the thermal expansion due to the variation of T_c with composition, using the data of Fine and Ellis[17].

Figure 2 shows the composition dependence of T_c observed by Asano *et al.*, for α -CoFe at atmospheric pressure in the 40 to 60 at.%

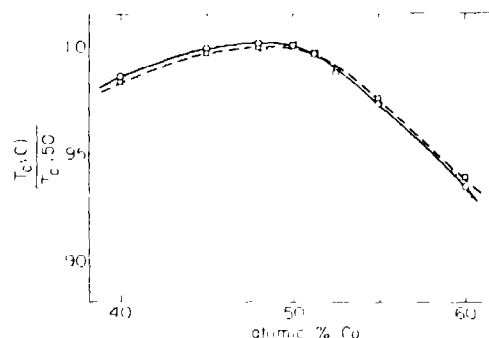


Fig. 2. Composition dependence of T_c . Squares are results of Asano and co-workers (Ref. [10]). The circles indicate our estimates of the critical temperature at a fixed lattice constant corresponding to that of α -CoFe containing 50 at.% Co at its T_c and atmospheric pressure. The dotted line gives the calculated values of Bienenstock and Lewis (Ref. [5]).

the asymmetry in the composition dependence of both observed and corrected T_c 's is quite evident. This contradicts the symmetrical composition dependence of T_c predicted by the Ising model with composition-independent pairwise interactions of all ranges. We therefore conclude that any model based on pairwise interaction energies that are independent of composition is insufficient to describe the order-disorder transformation of α -CoFe over the composition range in which it is observed.

Some evidence for variation of the interaction energies with composition may be

seen in the observations of Collins and Forsyth that the magnetic moment on the Fe atoms increases with increasing Co concentration in α -CoFe, while the moment on the Co atoms remains constant[18]. Unfortunately, the exact connection between magnetization and ordering is not understood, despite some attempts to include magnetic interactions in describing this transition [19, 20].

Since the corrections of the observed T_c 's to the case of constant lattice parameter are small, even very large uncertainties in the experimental value of $\delta T_c/\delta P$ or the estimated values of the compressibility and thermal expansion will not alter our conclusions. The assumption that $\delta \ln T_c/\delta \ln a$ is independent of composition is more serious. However, one would need an order of magnitude change of $\delta \ln T_c/\delta \ln a$ and a reversal of its sign with small composition changes near stoichiometry if the corrected T_c 's were to show symmetric composition dependence. We believe that such a drastic composition dependence of $\delta \ln T_c/\delta \ln a$ is unlikely since we observed no composition dependence of $\delta T_c/\delta P$ in our samples with 51, 52 and 52.5 at.% Co.

Finally, the large difference between the values of $\delta \ln T_c/\delta \ln a$ in α -CoFe (-1.5) and β -CuZn (-8.0) should be noted. Although there have been several attempts at theoretical calculations of the ordering energies in these alloys[21-23], they are not sufficiently developed to allow a meaningful discussion of this comparison at the present time.

Acknowledgements - The authors wish to thank Dr. S. G. Fishman for providing the CoFe samples and

Professor D. Lazarus for helpful comments and discussions.

REFERENCES

1. DIETRICH O. W. and ALS-NIELSEN J., *Phys Rev.* **153**, 711, 717 (1967).
2. ASHMAN J. and HANDLER P., *Phys Rev. Lett.* **23**, 642 (1969).
3. DOMB C. and DALTON N. W., *Proc. phys. Soc. Lond.* **89**, 859 (1966).
4. FAN C. and WU F. Y., *Phys. Rev.* **179**, 560 (1969).
5. BIENENSTOCK A. and LEWIS J., *Phys. Rev.* **160**, 393 (1967).
6. YOON D. N. and BIENENSTOCK A., *Phys. Rev.* **170**, 631 (1968).
7. See, e.g., NIX F. C. and SHOCKLEY W., *Rev. mod. Phys.* **10**, 63 (1938).
8. SHULL C. G. and SIEGEL S., *Phys. Rev.* **75**, 1008 (1949).
9. LYASHCHENKO B. G., LITVIN D. F. and ABOV Yu. B., *Soviet Phys. Crystallogr.* **6**, 443 (1962).
10. ASANO H., BANDO Y., NAKANISHI N. and KACHIS, *Trans. Japan Inst. Metals* **8**, 180 (1967).
11. GEITING I. C. and KENNEDY G. C. Publication 831, Institute of Geophysics and Planetary Physics, UIC, in preprint form. Work originally presented at NBS Geophysical Laboratory Symposium on high pressure calibration problems (1968).
12. BRIDGMAN P. W., *Proc. Am. Acad. Arts Sci.* **84**, 131 (1957).
13. GUINAN M. W. and BESHERS D. N., *J. Phys. Chem. Solids* **29**, 541 (1968).
14. LEESE J. and LORD A. F., Jr., *J. appl. Phys.* **39**, 3986 (1968).
15. McMANUS G. M., *Phys. Rev.* **129**, 2004 (1963).
16. ARIMAN R. A., *J. appl. Phys.* **23**, 475 (1952).
17. FINE M. F. and ELLIS W. C., *Trans. AIME* **175**, 742 (1948).
18. COLLINS M. F. and FORSYTH J. B., *Phil. Mag.* **8**, 401 (1963).
19. FGUCHI T., KINOSHITA C., Kiyoto S. and YASUTAKE K., *Japan. J. appl. Phys.* **5**, 645 (1966).
20. FGUCHI T., MATSUDA H. and OKI K., *IEEE Trans. Mag.* **MAG-4**, 476 (1968).
21. MOULIN F., *Proc. Phys. Soc. Lond.* **49**, 258 (1937).
22. HARRISON R. J. and PASKIN A., *J. Phys. Radium* **23**, 613 (1962).
23. LOMER W. M. (To be published)

MAGNETIC SUSCEPTIBILITY OF EUROPIUM TRIFLUORIDE

S. KERN

Department of Physics, Colorado State University, Fort Collins, Colo. 80521, U S A.

P. M. RACCAH*

Lincoln Laboratory, M.I.T. Lexington, Mass. 02173, U.S.A.

and

A. TVETEN

Department of Physics, Colorado State University, Fort Collins, Colo. 80521, U S A.

(Received 26 January 1970)

Abstract—Our previous measurement of the magnetic susceptibility of Europium Trifluoride from liquid helium to room temperature has been extended to 750°K. With the aid of the recent spectroscopically determined values of the low-lying energy levels of EuF_3 , a simple crystal field analysis has been used to calculate the expected temperature variation of the susceptibility. When an accurate account is taken of the sample impurities, the calculated and experimental values agree to within approximately 1 per cent over the entire region of measurement.

1. INTRODUCTION

BECAUSE of its unique electronic ground configuration among the rare earth ions, a magnetic singlet with a nearby triplet, the trivalent europium ion has proved to be a popular probe for investigating cooperative and covalent effects[2] that occur for the earth series. In an attempt to see how well recent spectroscopic data of Caspers, Fry and Fry[3] on EuF_3 could be used to predict the magnetic susceptibility of this strongly ionic compound, we have extended our previous helium to room temperature measurements[4] to 750°K. A straightforward application of crystal field theory[5] has enabled us to determine the crystal field eigen-functions of the ${}^3F_4$ excited multiplet; because the susceptibility becomes rapidly insensitive to the details of the energy level structure for this ion we have only roughly estimated the crystal field eigen-functions for the ${}^3F_2$ multiplet, ignored the splitting for higher J -states and used average values for the multiplet

energies as determined from the data of Caspers *et al.* This degree of approximation has proven sufficient to explain the variation of the susceptibility of EuF_3 to within experi-

mental error. The sample used showed small amounts of inert impurities (not approximately 1000 parts per million of sodium (see Table 1). The presence of the latter leads to the formation of NaEuF_4 (with europium in a divalent state) matrix and, there-

Table 1. Impurity content of EuF_3 sample

Na	10 ³ ppm	Si	100
O	200	Cl	100
N	300	K	5
C, Li	1	Ca	20
Y	1	Sc	1
Al	200		

*The Lincoln Laboratory portion of this work was sponsored by the Department of the Air Force.

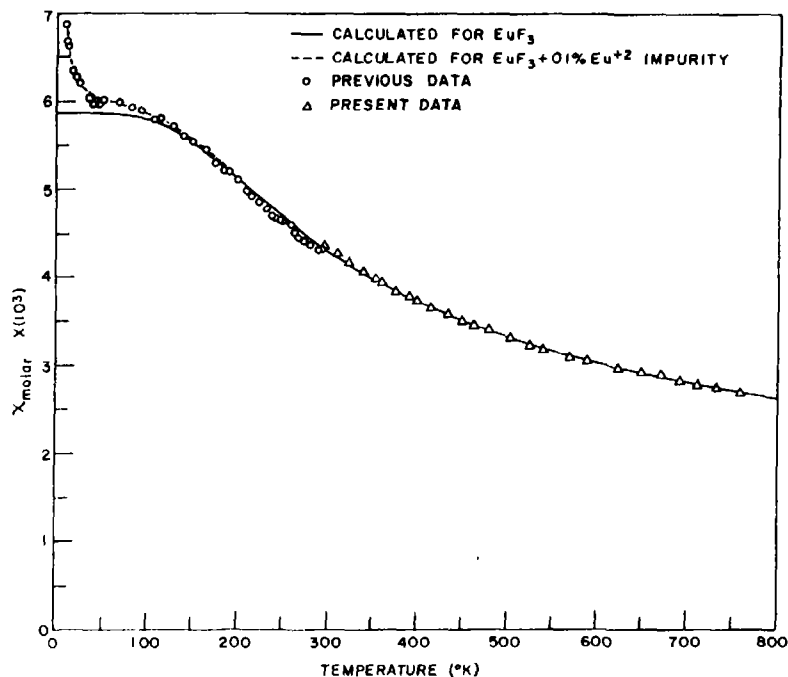


Fig. 1. Molar magnetic susceptibility of europium trifluoride vs. temperature.

fore, constitutes the only impurity considered important in its effect upon the susceptibility.

The high temperature measurements were performed with a Princeton Applied Research Model FM-1 vibrating sample magnetometer, with a Model FM-151 oven attachment. This latter had to be firmly mounted to suppress background signal from interfering with the measurements. With samples of about 0.1 g the background amounted to about 2 per cent of the sample signal but was field independent; it, therefore, could be fairly accurately accounted for and did not cause more than a small uncertainty. The results are shown in Fig. 1.

3. CALCULATIONS

In the usual way for a crystal field[5] calculation we assume that the potential for an electron on the cation can be expanded as

$$V = \sum_{n,m} A_n U_n^m(\theta, \phi) \quad (1)$$

where the $U_n^m(\theta, \phi)$ are tensor operators and the A_n^m are parameters that account for the strength of the crystal field[5]. The ground state for Eu^{+3} , ${}^7F_0$, is a singlet and can be considered as unaffected by the crystal field. The first excited state is the triplet, ${}^7F_1$, which is split by the second order terms in the expansion represented by equation (1) into three singlets which may be represented in $|JM\rangle$ notation as,

$$\begin{aligned} |1a\rangle &= |1, 0\rangle \\ |1b\rangle &= \frac{1}{\sqrt{2}} [|1, 1\rangle + |1, -1\rangle] \\ |1c\rangle &= \frac{1}{\sqrt{2}} [|1, 1\rangle - |1, -1\rangle] \end{aligned} \quad (2)$$

where the states on the left hand side are given by the free ion J value from which the crystal field state is derived. Ignoring 4th order terms, the same 2nd order parameters derived from

the ${}^7F_1$ splittings were applied to the ${}^7F_2$ multiplet to approximately determine its crystal field eigenfunctions.

The susceptibility from 0 to 800°K was then calculated using [6]

ed line in the figure is the sum of the calculated results plus the contribution of the 0.1% of Eu^{+2} present. The magnitude of this contribution is computed by a simple Curie dependence for the Eu^{+2} susceptibility, a reasonable

$$X = \frac{N\beta^2}{3} \sum_j \left\{ \frac{\langle LSJM | \mathbf{M}_k^q | LSJM \rangle^2}{kT} - 2 \sum_{J'M'} \frac{\langle LSJM | \mathbf{M}_k^q | L'S'J'M' \rangle^2}{E_{JM}^\circ - E_{J'M'}^\circ} \right\} (2J+1) e^{-E_j/kT} \quad (3)$$

$$\sum_j (2J+1) e^{-E_j/kT}$$

with

$$\langle LSJM | \mathbf{M}_k^q | L'S'J'M' \rangle = (-1)^{J-M} \begin{pmatrix} J & k & J \\ -M & q & M' \end{pmatrix} \langle LSJ | \mathbf{M}_k | L'S'J' \rangle \quad (4)$$

where

$$\begin{aligned} \langle LSJ | \mathbf{M}_k | L'S'J' \rangle &= \langle 1_a 1_b S I J | | \mathbf{L} + 2\mathbf{S} | | 1_a 1_b S' I' J' \rangle = \delta_{S,S'} \sqrt{(2J+1)(2J'+1)(2L'+1)} \\ &\times (-1)^{1_a+1_b+S+J'} \begin{Bmatrix} S & L & J \\ 1 & J' & L' \end{Bmatrix} \left[(-1)^{L'-L} \begin{Bmatrix} 1_a & 1_b & L \\ 1 & L' & 1_a \end{Bmatrix} \langle L_a | | \mathbf{L} | | 1_a \rangle \right. \\ &+ \left. \begin{Bmatrix} 1_a & 1_b & L \\ 1 & L & 1_b \end{Bmatrix} \langle 1_b | | \mathbf{L} | | 1_b \rangle \right] + 2\delta_{S,S'} \sqrt{(2J+1)(2J'+1)(2S+1)S(S+1)} \\ &\times (-1)^{1+L+J+J'} \begin{Bmatrix} L & S & I \\ 1 & J' & S \end{Bmatrix} \end{aligned} \quad (5)$$

for the ${}^7F_0$ and ${}^7F_1$ multiplets, and the Van Vleck formula [7] for the upper states. The results of this calculation are given in Table 1 and plotted as the solid line in Fig. 1; the dashed

Table 2. Calculated magnetic susceptibility of EuF_3

T (°K)	χ (cgs units)
0	5.88 (10^{-3})
50	5.88
100	5.80
150	5.53
200	5.11
250	4.69
300	4.32
400	3.73
500	3.34
600	3.05
700	2.82
800	2.65 (10^{-3})

and would, perhaps, appear as a magnetic standard which is both easy to prepare, and chemically stable in air over a wide temperature region. In view of the current high interest in the magnetic behavior of Europic compounds, further refinements in the calculations, involving crystal-field and spin-orbit mixing effects, are presently in progress.

REFERENCES

1. HUANG N. L. and VAN VLECK J. H., *J. appl. Phys.* **40**, 1144 (1969).
2. BURNS G. and AXFORD J. D., *Optical Properties of Ions in Crystals* (Edited by H. M. Grosswhite and H. W. Moos), Interscience, New York (1967).

3. CASPERS H. H., RAST H. F. and FRY J. L., *J. chem. Phys.* **47**, 4505 (1967).
4. KERN S. and RACCAH P. M., *J. Phys. Chem. Solids* **26**, 1625 (1965).
5. HUTCHINGS M. T., *Solid State Physics* (Edited by F. Seitz and D. Turnbull), Vol. 16 Academic Press, New York (1964).
6. SHORE B. W. and MENZEL D. H., *Principles of Atomic Spectra*, p. 363. Wiley, New York (1968). Their equation on p. 363 is missing a factor of 2 in front of the second $\delta_{ss'}$ term.
7. VAN VLECK J. H., *The Theory of Electric and Magnetic Susceptibilities*, p. 233. Oxford Universities Press (1932).

SUPERTRANSFERRED HYPERFINE FIELDS ON TETRAHEDRAL SITES IN SOME CHROMIUM SULPHO- AND SELENO SPINELS

P. R. LOCHER and R. P. VAN STAPELE

Philips Research Laboratories, N. V. Philips' Gloeilampenfabrieken, Eindhoven-Netherlands

(Received 19 January 1970)

Abstract—Nuclear magnetic resonance of ^{63}Cu , ^{65}Cu and ^{115}In in semiconducting sulpho- and seleno-spinels of the type $\text{Cu}_{0.5}^{1+}\text{A}_{0.5}^{3+}[\text{B}_2^{3+}]\text{X}_4$ with $\text{A} = \text{In}$ or Fe and $\text{B} = \text{Cr}$ or Rh revealed the existence of large supertransferred hyperfine fields on the nuclei of diamagnetic ions on tetrahedral sites. It is remarkable that, in terms of spin densities in the first empty s shell of the diamagnetic ion, these fields are of comparable magnitude.

1. INTRODUCTION

IN THE past few years NMR on tetrahedrally coordinated Cu in sulphospinels has been measured in the metallic conducting spinels $\text{Cu}[\text{Cr}_2]\text{X}_4$ ($\text{X} = \text{S}$, Se and Te) [1-5]. In these ferromagnets the experimentally observed total magnetization of $5 \mu_B$ per formula unit [6] results from a moment between 5 and $6 \mu_B$ localized on the Cr ions [7] and a corresponding negative polarization of the band in which the conduction occurs [8, 9]. The hyperfine field on the Cu nucleus will generally originate in two kinds of mechanisms [10]: (a) indirect interaction of the Cu nuclear spin with the band polarization, and (b) interactions directly between the Cu nuclear spin and the moments of the Cr d electrons (supertransferred hyperfine fields). In order to study separately the supertransferred hyperfine fields on Cu due to the Cr spins one needs semiconducting spinels with Cu on tetrahedral sites. Attempts to observe Cu NMR in semiconducting compounds such as $\text{Cu}[\text{CrTi}]\text{S}_4$ failed, probably because the Cu resonances were strongly inhomogeneously broadened by the statistical distribution of Cr^{3+} and Ti^{3+} present on the octahedral sites. A much more favourable situation occurs in the semiconducting spinels of the type $\text{Cu}_{0.5}^{1+}\text{A}_{0.5}^{3+}[\text{B}_2^{3+}]\text{X}_4^{2-}$ with $\text{X} = \text{S}$ and Se , $\text{A} = \text{Fe}$ or In and $\text{B} = \text{Cr}$ or Rh [11-14].

In these compounds the monovalent Cu ions and the trivalent A ions are ordered on the tetrahedral sites [12], with the consequence that the perfect cubic symmetry of the tetrahedral sites in the spinel lattice is conserved in the mixed crystal. Cu nuclear resonances are indeed easily observable in these compounds. The supertransferred hyperfine

fields also allow trivalent diamagnetic ions to be substituted on tetrahedral sites. Using this possibility the hyperfine fields on the nucleus of trivalent In on tetrahedral sites due to Cr^{3+} on octahedral sites have also been measured.

2. SUBSTANCES

The powdered substances are those prepared by Lotgering and used for susceptibility measurements [12, 14]. The susceptibilities handled in the analysis of the NMR line shifts are taken from that work. They have not been corrected for diamagnetism.

For $\text{Cu}_{0.5}\text{Fe}_{0.5}[\text{Cr}_2]\text{S}_4$, the susceptibility values are close to those published by Haacke and Beegle[11].

For $\text{Cu}_{0.5}\text{In}_{0.5}[\text{Cr}_2]\text{S}_4$, Lotgering's data are similar to those published recently by Yokoyama and Chiba[13] who measured from 77 up to 380°K and found a Curie constant of $C_M = 3.8 \pm 0.2^\circ\text{K cm}^3/\text{mole}$ and an asymptotic Curie temperature of $\theta = +135 \pm 5^\circ\text{K}$. From measurements up to 1000°K, Lotgering found the somewhat different values of $C_M = 3.4 \pm 0.1^\circ\text{K cm}^3/\text{mole}$ and $\theta = +105 \pm 5^\circ\text{K}$. X-ray data indicate a small amount of second phase, CrSe, as well as extra reflections[12] typical of ionic ordering of In and Cu on A-sites. These extra lines have not been mentioned by Yokoyama and Chiba.

3. EXPERIMENTAL METHODS

Most measurements were done only in the paramagnetic state of the substances, using external fields of around 10 kOe and a modified Pound-Knight-Watkins oscillator [17].

We studied the ferrimagnetic compound $\text{Cu}_{0.5}\text{Fe}_{0.5}[\text{Cr}_2]\text{S}_4$ also in the ordered magnetic state, at zero external field H_0 . For this case, a frequency-modulated oscillator of the Collpitt type was used, while the lock-in detection was at either the first or the second harmonic of the frequency of modulation, this latter frequency being for instance 15 Hz. A vibrating small capacitor provided this modulation and a motor drive on the tuning capacitor was used for the slow frequency sweep. Figure 1 gives a result at 77°K. A special glass dewar with a liquid-helium cold finger was used for the zero-field NMR at 2 to 4°K. The NMR coil, consisting of one turn only, was arranged around the outside of this cold finger which contained the sample-holder. In order to obtain a reasonably high filling factor, the tip, 5 cm in length, does not have a liquid nitrogen screening. The inner diameter of the tip is 12 mm and the outer diameter is 20 mm. A styrofoam box in which cold nitrogen gas was blown provided a temperature around the tip

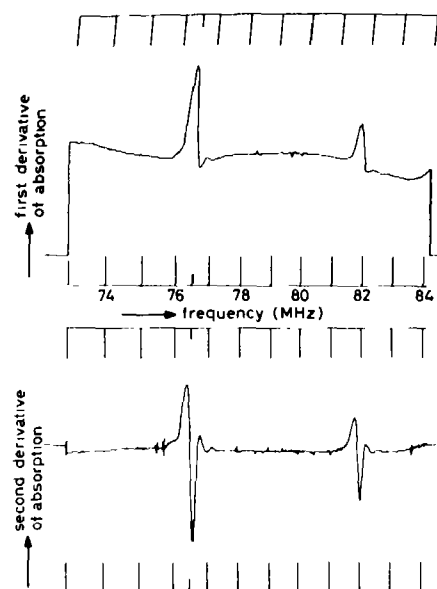


Fig. 1 NMR lines of ^{63}Cu and ^{65}Cu at zero external static magnetic field in ferrimagnetic $\text{Cu}_{0.5}\text{Fe}_{0.5}\text{Cr}_2\text{S}_4$, as a function of the frequency of the marginal oscillator. The frequency modulation used had a modulation frequency of 14 Hz and a peak-to-peak depth varying from 85 to 102 kHz at 76 and 82 MHz respectively. The upper picture gives the oscillator amplitude, lock-in detected at 14 Hz, and the lower picture gives the same quantity at 28 Hz. In the first case, a large spurious base-line shift is detected. A double RC filter with a time constant of 1 sec was used, and the recording took 30 min.

of 150°K. Due to this precaution, the helium evaporation decreased from 0.6 to 0.1 litres of liquid per hour.

The measurements in the paramagnetic state were done using field modulation of about the line width or somewhat less, and using conventional lock-in detection. The signal-to-noise ratios were seldom better than 10 in a half-hour run. No signs of saturation of the resonance lines have been observed, except possibly in the compounds that do not contain paramagnetic ions, such as $\text{Cu}_{0.5}\text{Ga}_{0.5}[\text{Rh}_2]\text{S}_4$.

An oven around the NMR coil provided temperatures up to 500°C. The powder samples were contained in sealed pyrex tubes and then inserted into the NMR coil.

The static magnetic fields were measured with an accuracy of $1:10^5$, using the NMR of protons in water. A gyromagnetic ratio of $42.5759 \text{ MHz}/10 \text{ kOe}$ [18] was used for calculating the fields from the proton NMR frequencies.

4. NMR RESULTS

In paramagnetic substances, a NMR line is expected to be observable under favourable conditions such as a sufficiently rapid exchange frequency for the paramagnetic ions, and only small nuclear electric quadrupole interactions. The NMR frequency ω may then be expressed as

$$\omega = \gamma_n [H_0 + \delta H + \alpha M_p(T)] \quad (1)$$

in which γ_n is the gyromagnetic ratio of the bare nucleus, H_0 is the applied static magnetic field, $M_p(T)$ is the temperature-dependent part of the paramagnetic magnetization, $\alpha M_p(T)$ is the temperature-dependent part of the (small) extra field at the nucleus, and δH stands for the remaining extra field at the nucleus. The term δH contains contributions

connected with diamagnetism and with Van Vleck paramagnetism. The last term has the simple form $\alpha M_p(T)$, α being constant, provided there is only one kind of paramagnetic ion interacting with the nuclei. The two terms, δH and $\alpha M_p(T)$ are proportional to H_0 , so that one may write

$$\omega = \gamma_{\text{eff}} H_0 \quad (2)$$

in which

$$\gamma_{\text{eff}} = \gamma_n [1 + \delta H/H_0 + \alpha \chi_p(T)]. \quad (3)$$

The effective gyromagnetic ratio γ_{eff} is directly obtained from the NMR measurements. By plotting γ_{eff} vs. the molar susceptibility χ_M , it is possible to check the linear relation (3), since χ_M is the sum of the temperature dependent susceptibility $\chi_p(T)$ and the temperature independent diamagnetic and Van Vleck susceptibility. The constant α can then be derived from the slope $\gamma_n \alpha$, using the well-known value of γ_n . This procedure is followed in the Figs. 2-5. Resulting

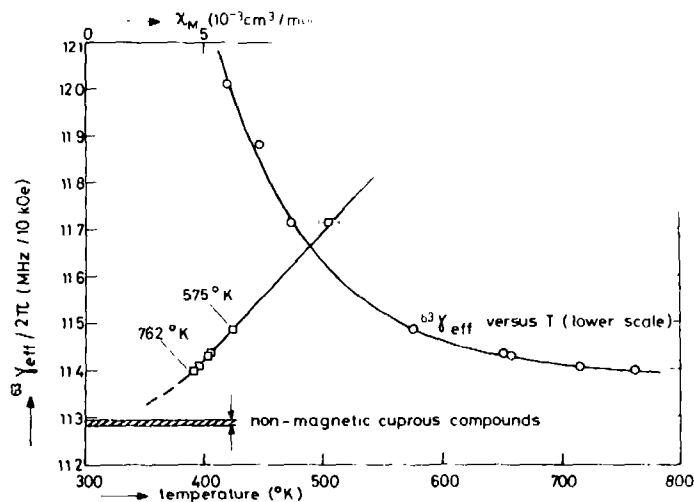


Fig. 2 The effective gyromagnetic ratio γ_{eff} of ^{63}Cu , characterizing the NMR line position, in paramagnetic $\text{Cu}_0, \text{Fe}_0, \text{Cr}_2\text{S}_4$, as a function of temperature and as a function of the molar susceptibility

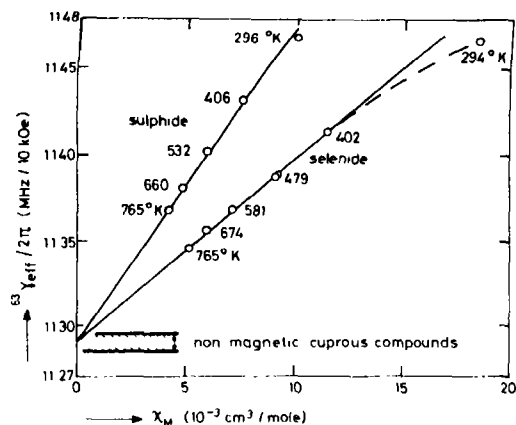


Fig. 3. The γ_{eff} values of ^{63}Cu in paramagnetic $\text{Cu}_{0.5}\text{In}_{0.5}\text{Cr}_2\text{X}_4$ with $\text{X} = \text{S}$ or Se , plotted as a function of the molar susceptibility

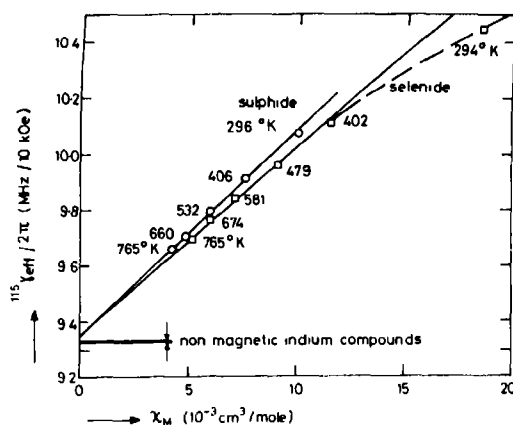


Fig. 4. The γ_{eff} values of ^{115}In in paramagnetic $\text{Cu}_{0.5}\text{In}_{0.5}\text{Cr}_2\text{X}_4$ with $\text{X} = \text{S}$ or Se , plotted as a function of the molar susceptibility

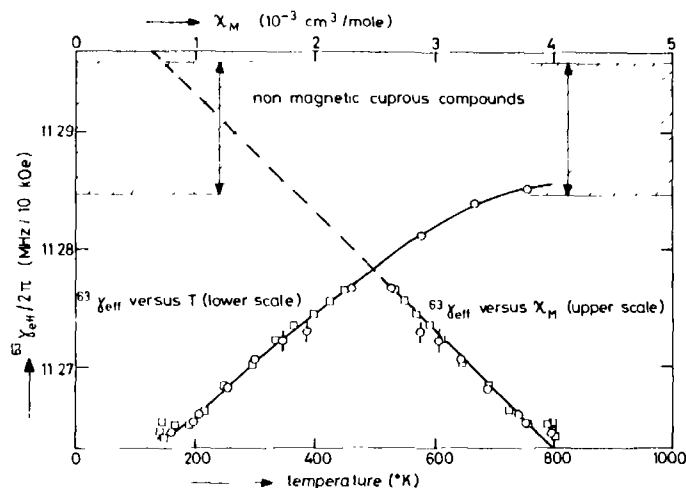


Fig. 5. The γ_{eff} values of ^{63}Cu in paramagnetic $\text{Cu}_{0.5}\text{Fe}_{0.5}\text{Rh}_2\text{S}_4$, plotted as a function of temperature and as a function of the molar susceptibility. The points (○) and (□) correspond to NMR in two samples prepared in a slightly different way, the susceptibilities having always been taken from the best sample.

Table 1, together with approximate values of the measured NMR line width. For $\text{Cu}_{0.5}\text{Fe}_{0.5}[\text{Cr}_2|\text{S}_4]$ (Fig. 2), the linear relation (3) is actually not expected to be valid since there are two kinds of magnetic ion, Fe^{3+} and Cr^{3+} , in this substance. This case will be discussed below. The Figs. 3 and 4 give the

results for $\text{Cu}_{0.5}\text{Cr}_2|\text{X}_4$ with $\text{X} = \text{S}$ and Se . In Figs. 2–4, the γ_{eff} values increase with increasing χ (so-called positive line shift). For $\text{Cu}_{0.5}\text{Fe}_{0.5}[\text{Rh}_2|\text{S}_4]$ (Fig. 5) the NMR line shifts are negative and comparatively small. When lowering the temperature, the NMR line of ^{63}Cu disappears rather suddenly which

Table 1. The slopes of the lines in Figs. 2-5, given by the quantity $\alpha = (1/\gamma_n)d\gamma_{\text{eff}}/d\chi_M$, and approximate values of the line width between the extremes of the absorption derivative

Compound	Fig.	α_{Cu} (mole/cm ³)	α_{In} (mole/cm ³)	Line width (Oe)	
				⁶³ Cu	¹¹⁵ In
Cu _{0.5} Fe _{0.5} [Cr ₂]S ₄	2	$+3.7 \pm 0.4$ (for 420-470°K)	—	20-30	—
Cu _{0.5} In _{0.5} [Cr ₂]S ₄	3,4	+1.63	+7.9	7	30
Cu _{0.5} In _{0.5} [Cr ₂]Se ₄	3,4	+10.95	+7.3	8	40
Cu _{0.5} Fe _{0.5} [Rh ₂]S ₄	5	-0.89	—	2	—

is undoubtedly due to the transition to anti-ferromagnetic ordering of the Fe³⁺ spins [14]. At 140°K the line is only a little weaker than at higher temperatures. At 136°K it is some 10 times weaker and barely observable. From our observations it can be concluded that the Néel temperature is below 135°K. Although not much, this value is clearly below the minimum in the χ_M^{-1} vs. $-T$ curve [14].

In the Figs. 2-5 we plotted γ_{eff} values instead of the more commonly used line shifts $(\gamma_{\text{eff}} - \gamma_{\text{ref}})/\gamma_{\text{ref}}$ with respect to a diamagnetic reference substance having a gyromagnetic ratio γ_{ref} . The reason why we preferred to plot γ_{eff} is the comparatively large spread of the different possible γ_{ref} values for Cu. Table 2 lists such values for compounds that are diamagnetic or perhaps weakly paramagnetic, the susceptibility being independent of temperature. For convenience, these compounds will briefly be called non-magnetic. Their range of γ_{eff} values is indicated in Figs. 2-6, for ⁶³Cu as well as for ¹¹⁵In. In Fig. 6, the data of Fig. 3 and 4 are given in a different way: the γ_{eff} values of ¹¹⁵In are plotted as a function of the corresponding values of ⁶³Cu, the temperature being the implicit parameter. This figure illustrates the accuracy of measurement apart from inaccuracies in the temperatures and susceptibilities. For increasing temperature, one expects $\chi_p(T)$ to approach zero and the measured molar susceptibility χ_M to approach a temperature-

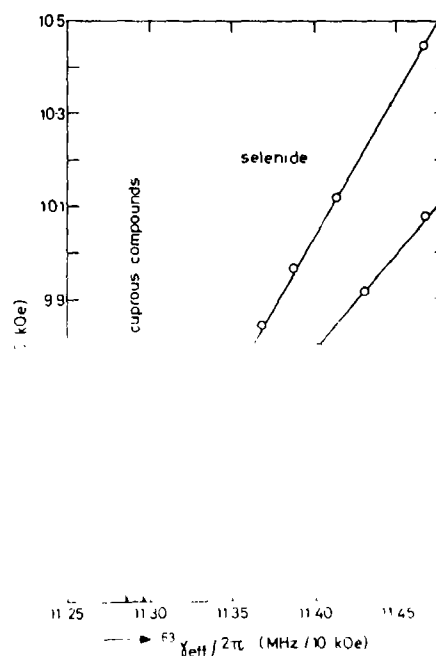


Fig. 6. The γ_{eff} values of ¹¹⁵In plotted as a function of the corresponding γ_{eff} values of ⁶³Cu, in paramagnetic Cu_{0.5}In_{0.5}Cr₂X₄ with X = S or Se. The temperature is the implicit parameter.

independent value $\chi_M(\infty)$. In Figs. 2-5, the extrapolated γ_{eff} value at $\chi_M = \chi_M(\infty)$ equals $\gamma_n(1 + \delta H/H_0)$ according to (3). This value is expected to be comparable in magnitude with the γ_{eff} values for the non-magnetic compounds. We estimate $|\chi_M(\infty)|$ to be not

Table 2. NMR line positions in non-magnetic semiconducting compounds

Compound	Nucleus	Temperature (°K)	$\gamma_{\text{eff}}/2\pi$ (MHz/10 kOe)	Ref.
CuCl	^{63}Cu	295 and 77	11.2853 ± 0.0002	[a]
CuInFe ₂	^{63}Cu	295 and 77	11.2900 ± 0.0005	[a, b]
CuInSe ₂	^{63}Cu	295	11.2920 ± 0.0005	[a, b]
		77	11.2927 ± 0.0005	[a, b]
Cu ₄ VS ₄	^{63}Cu	295	11.2964 ± 0.0015	[a, b]
Cu _{0.5} Ga _{0.5} [Rh ₂]S ₄	^{63}Cu	295	11.2910 ± 0.0002	[a]
	^{63}Cu	77	11.2917 ± 0.0002	[a]
Cu _{0.5} In _{0.5} [Rh ₂]S ₄	^{63}Cu	295	11.2921 ± 0.0002	[a]
	^{63}Cu	77	11.2923 ± 0.0002	[a]
	^{115}In	77	9.3316 ± 0.0005	[a]
Cu _{0.5} In _{0.5} [In ₂]S ₄	^{63}Cu	295 and 77	not observable	[a]
	^{63}Cu	4.2 and 1.5	11.28 ± 0.02 (very broad)	[a]
	^{115}In	4.2	not observable	[a]
In-nitrate } solution }	^{115}In	295	9.3296 ± 0.0009	[c]
			9.3284 ± 0.0006	[d]
InSb	^{115}In	295 and 77	9.329 ± 0.003	[e]

[a] This work.

[b] Ref. [5].

[c] PROCTOR W. G. and YU F. C., *Phys. Rev.* **81**, 20 (1951).[d] TING YU and WILLIAMS D., *Phys. Rev.* **89**, 595 (1953).[e] SHUI MAN R. G., MAYES J. M. and MCCALL D. W., *Phys. Rev.* **100**, 692 (1955).

much more than $0.2 \times 10^{-3} \text{ cm}^3/\text{mole}$. In Fig. 3 and 4 one obtains reasonable extrapolated γ_{eff} values at possible values of $\chi_M(\infty)$. In Fig. 5 the extrapolated value of $^{63}\gamma_{\text{eff}}$ at $\chi_M(\infty)$ is 11.302 MHz/10 kOe (or even somewhat larger) which is surprisingly high. Such a high value is also obtained, without using any susceptibility data, by means of an extrapolation technique in which γ_{ref} is determined in such a way as to make $(\gamma_{\text{eff}} - \gamma_{\text{ref}})^{-1}$ vs. $-T$ a straight line. Perhaps, a temperature dependence of the hyperfine interaction parameter α is the cause of the unexpected result of the extrapolation.

For $\text{Cu}_{0.5}\text{Fe}_{0.5}[\text{Cr}_2]\text{S}_4$ (Fig. 2), a naive straight-line extrapolation to $\chi_M(\infty)$ would

yield a γ_{eff} value for ^{63}Cu of below 11.2 MHz/10 kOe which is inconceivably low. As remarked before, relation (3) is not expected to be valid, since both Cr and Fe contribute to the Cu line shift and to the susceptibility, but the relative importance of Cr and Fe is different in these two quantities. No attempt to analyse this quantitatively will be given here, but qualitatively the behaviour can be understood, using a model in which the main contribution to the Cu hyperfine field arises from the Cr *d*-electron spins and in which the contributions of Cr and Fe to the susceptibility are still opposite to each other at temperatures slightly above T_c (400–500°K), whereas their contributions add at very high tempera-

tures (above 1000°K)[19]. In this picture, the α -value for temperatures slightly above T_c (Table 1) is the best one can take for making a rough prediction of the hyperfine field at Cu in the ferrimagnetic state at 0°K. Taking the saturation magnetization M_s instead of the paramagnetic magnetization M_p in (1), one calculates a hyperfine field of $H_{hf} = \alpha M_s = (3.7 \pm 0.4) \times 19.5 = 72 \pm 7$ kOe. Here we took $M_s = 19.5$ kOe cm³/mole, corresponding to the theoretical moment per formula unit of $2 \times 3 - \frac{1}{2} \times 5 = 3.5$ Bohr magnetons. Zero-field Cu NMR (Figs. 1 and 7) was indeed observed near the predicted frequency. It yields $H_{hf} = 68.8 \pm 0.2$ kOe at 0°K. Probably, the observed zero-field resonances originate from nuclei in the domain walls. A so-called pulling[20] of the NMR frequency may exist in such a case where the electron spin and nuclear spin motions are severely coupled. In our case there is apparently no important pulling since at 4°K we found the ratio of the resonance frequencies of ⁶⁵Cu and ⁶³Cu to be equal to the known ratio of the gyromagnetic ratios γ_n of these nuclei, within

the accuracy of measurement of 0.1 per cent. Also, the resonance frequencies of ⁶⁵Cu at 2 and 4°K are equal within 0.05 per cent. In Fig. 7 the Cu hyperfine field is plotted as a function of temperature, together with the total magnetization and the Fe sublattice magnetization, as measured by Van Wieringen [12] from the Mössbauer spectra. From this data the strength of the coupling between the Cu nuclear spin and the Cr *d*-electrons can be calculated (see next section).

5. DISCUSSION

To compare the strength of the hyperfine fields in the different compounds we calculate their values for the magnetic saturation. If we use a theoretical moment of $M_s = 33.5$ kOe cm³/mole for 2 Cr³⁺ per molecule and a moment of $M_s = 14.0$ kOe cm³/mole for $\frac{1}{2}$ Fe³⁺ per molecule, we calculate the values $H_{hf} = \alpha M_s$ given in Table 3 from the values of α given in Table 1.

At first we compare the hyperfine field on the Cu nucleus in the sulphides. In the ferrimagnet Cu_{0.5}Fe_{0.5}[Cr₂]S₄ the moment of the

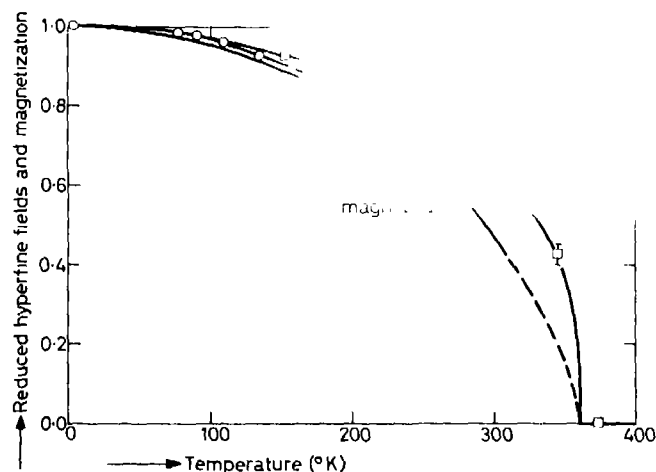


Fig. 7 The temperature dependence of the total magnetization and of the hyperfine fields on Fe and Cu in ferrimagnetic Cu_{0.5}Fe_{0.5}Cr₂S₄. At zero temperature, the magnetization is 3.2 μ_B and the hyperfine fields on Fe and Cu are 385 kOe (see Ref. [12]) and 68.8 $\pm$ 0.2 kOe respectively

Table 3. Hyperfine fields on nuclei of diamagnetic ions on tetrahedral sites in chalcogenide spinels, scaled by the hyperfine fields in the corresponding $nd^{10}(n+1)s^1$ configuration

Nucleus and ion	Electron config	hf field (kOe) in $nd^{10}(n+1)s^1$	Ref	Compound	H_h (kOe)	Ref.	Spin density in $(n+1)s$ (%)
$^{63}\text{Cu}^{1+}$	$3d^{10}$	2.598×10^3	[a]	$\text{Cu}_0^{1+}\text{In}_{0.5}^{3+}\text{Cr}_{2.5}^{3+}\text{S}_4$ $\text{Cu}_0^{1+}\text{Fe}_{0.5}^{3+}\text{Rh}_{2.5}^{3+}\text{S}_4$ $\text{Cu}_0^{1+}\text{Fe}_{0.5}^{3+}\text{Cr}_{2.5}^{3+}\text{S}_4$	+55 -12.5 +68.8 $\approx 12+56$	[e] [e] [e]	+2.1 — (+2.2)
				$\text{Cu}_0^{1+}\text{In}_{0.5}^{3+}\text{Cr}_{2.5}^{3+}\text{Se}_4$	-32	[e]	+1.2
$^{111}\text{Cd}^{2+}$	$4d^{10}$	8.2×10^3	[b]	$\text{Cd}^{2+}\text{Cr}_{2.5}^{3+}\text{S}_4$ $\text{Cd}^{2+}\text{Cr}_{2.5}^{3+}\text{Se}_4$	+168 +136	[f] [f]	+2.0 +1.7
$^{200}\text{Hg}^{2+}$	$5d^{10}$	26.8×10^3	[c]	$\text{Hg}^{2+}\text{Cr}_{2.5}^{3+}\text{S}_4$ $\text{Hg}^{2+}\text{Cr}_{2.5}^{3+}\text{Se}_4$	+524 +446	[f] [f]	+2.0 +1.7
$^{115}\text{In}^{1+}$	$4d^{10}$	11.7×10^3	[d]	$\text{Cu}_0^{1+}\text{In}_{0.5}^{3+}\text{Cr}_{2.5}^{3+}\text{S}_4$ $\text{Cu}_0^{1+}\text{In}_{0.5}^{3+}\text{Cr}_{2.5}^{3+}\text{Se}_4$	+266 +244	[e] [e]	+2.3 +2.1

[a] TING Y. and LEW H., *Phys. Rev.* **105**, 581 (1957)

[b] KELLY F. M. and SUTHERLAND J. B., *Can. J. Phys.* **34**, 521 (1956)

[c] MROZOWSKI S., *Phys. Rev.* **61**, 605 (1942)

[d] CAMPBELL J. S. and DAVIS J. R., *Phys. Rev.* **55**, 1125 (1939).

[e] This work.

[f] Ref. [15] and [16]

tetrahedral Fe sublattice is opposite to that of the octahedral Cr sublattice [12]. The temperature dependence of the moment of the Fe sublattice has been measured by Van Wieringen [12]. Measurement of the total magnetization as a function of temperature gave different results for different specimens, the value of the saturation magnetization being at least 8 per cent too low compared to the theoretical value. This is probably due to difficulties with the purity. However, the reduced magnetization $M(T)/M(0)$ as a function of temperature showed better reproducibility. Using theoretical values for the saturation magnetization of the sublattices, the Cr moment was calculated as a function of temperature from the total magnetization and the Fe magnetization. If we assume the coupling of the Cu nucleus to the Fe spins to be of the same negative sign and strength as in $\text{Cu}_{0.5}\text{Fe}_{0.5}|\text{Rh}_2|\text{S}_4$, the hyperfine field on Cu in $\text{Cu}_{0.5}\text{Fe}_{0.5}|\text{Cr}_2|\text{S}_4$ can be corrected for the small positive part due to the negative Fe magnetization. The strength of the coupling between the Cu nucleus and the Cr magnetization can then be calculated. The value of α turns out to be 1.67 ± 0.03 throughout the temperature interval $4 < 220^\circ\text{K}$, which value compares well with $\alpha = 1.63$ found in $\text{Cu}_{0.5}\text{In}_{0.5}|\text{Cr}_2|\text{S}_4$. In magnetic saturation the hyperfine field on $\text{Cu}_{0.5}\text{Fe}_{0.5}|\text{Cr}_2|\text{S}_4$ is then found to consist of $+56\text{ kOe}$ from the Cr magnetization and $+12.5\text{ kOe}$ due to the Fe magnetization (see Table 3).

The next point is the strength of the hyperfine field on the nuclei of the diamagnetic ions Cu^{1+} , Cd^{2+} , Hg^{2+} and In^{3+} on tetrahedral sites in spinels induced by the Cr moments on octahedral sites. Transfer of d electrons of the Cr ions to the first empty s shell of the non-magnetic ions [21] is thought to be one of the origins of the supertransferred hyperfine fields. On the basis of this idea Berger, Budnick and Burch [15] scaled the hyperfine fields as measured by them on the Cd^{2+} and Hg^{2+} nuclei in $\text{Cd}|\text{Cr}_2|\text{X}_4$ and $\text{Hg}|\text{Cr}_2|\text{X}_4$ ($\text{X} = \text{S}$ and Se) by taking the ratio to the

hyperfine field of the corresponding $4d^{10}5s^1$ and $5d^{10}6s^1$ configurations of Cd^{1+} and Hg^{1+} respectively. Extending this procedure to Cu and In, we obtain the spin densities presented in Table 3. We note that in the selenides the spin density on the diamagnetic ion increases regularly from 1.2 to 2.1 per cent going from monovalent Cu to trivalent In. However, a similar regular change with the charge of the diamagnetic ion is not observed in the sulphides, where the spin density on Cu^{1+} is rather large. The difference in spin density on the same diamagnetic ion in sulphides and in selenides is small (0.2–0.3 per cent) except for Cu^{1+} where it is 1 per cent.

A similar dependence on the nature of the ligand is also observed in the hyperfine fields on Cu in $\text{Cu}|\text{Cr}_2|\text{X}_4$ ($\text{X} = \text{S}$, Se and Te). In the magnetic saturation of these metallic conducting ferromagnets, a Cu hyperfine field of $+90\text{ kOe}$ was observed in the sulphide, $+72\text{ kOe}$ in the selenide and $+40\text{ kOe}$ in the telluride [1–5]. The hyperfine fields on Cu in the metallic conducting compounds apparently exceed the hyperfine fields in the correspond-

DISCUSSION

Cr d electrons to copper $4s$ states. If the strength of the last mechanism is the same as in semiconducting compounds containing divalent ions on the tetrahedral sites, we expect a supertransferred hyperfine field on Cu of 51 kOe in CuCr_2S_4 (corresponding to a spin density of 2.0 per cent on Cd^{2+} in CdCr_2S_4) and of 43 kOe in CuCr_2Se_4 (corresponding to 1.7 per cent in CdCr_2Se_4). This leaves 40 and 30 kOe for the hyperfine field on the Cu nucleus due to the polarization of the t_2^{2+} band in CuCr_2S_4 and CuCr_2Se_4 respectively. Such small numbers in a case where the

polarization corresponds to $1 \mu_B$ per Cu ion make it doubtful whether the t_2^{A*} states can be considered to have mainly copper 3d character[22]. Moreover there is strong evidence of monovalent copper in these compounds [8, 23]. Therefore we prefer to use the model in which the electrical conduction is attributed to holes in the valence band[8]. If one assumes the interactions between Cr d electrons and the nucleus of the monovalent copper to be of the same strength as in the semiconducting compounds, the extra contribution of 40 kOe to the hyperfine field observed in the metallic conducting compounds originates in the negative polarization of the valence band. A negative coupling between the magnetic polarization of the valence band and the Cu nucleus is also observed in the compounds $\text{Cu}[\text{Rh}_2\text{X}_4]$ ($\text{X} = \text{S}, \text{Se}$)[5, 8]. These compounds have a metallic electrical conduction and a temperature-independent paramagnetism[8, 24]. Van Vleck paramagnetism of the non-magnetic Rh^{3+} ions and Pauli paramagnetism of the valence band contribute to the magnetic susceptibility[8]. A negative Knight shift of the Cu nuclear resonance is observed both in the sulphide and the selenide[5].

Acknowledgements—We thank Dr. F. K. Lotgering for cordial cooperation, Mr. G. H. A. M. van der Steen for the preparation of the samples and Mr. W. M. Dam for technical assistance.

REFERENCES

1. YOKOYAMA H., WATANABE R. and CHIBA S., *J. phys. Soc. Japan* **22**, 659 (1967); *ibid* **23**, 450 (1967).
2. LOCHER P. R., *Solid State Commun.* **5**, 185 (1967).
3. BERGER S. B., BUDNICK J. I. and BURCH T. J., *Phys. Lett.* **26A**, 450 (1968).
4. KHOI LE DANG, *Solid State Commun.* **6**, 203 (1968).
5. LOCHER P. R., *Zts. für Angew. Phys.* **24**, 277 (1968).
6. LOTGERING F. K., *Proceedings of the International Conference on Magnetism*, p. 533. Nottingham, (1964).
7. COLOMINAS C., *Phys. Rev.* **153**, 558 (1967).
8. LOTGERING F. K. and VAN STAPELE R. P., *J. appl. Phys.* **39**, 417 (1968).
9. GOODENOUGH J. B., *J. Phys. Chem. Solids* **30**, 261 (1969).
10. WATSON R. E. and FREEMAN A. J., *Hyperfine interactions*, pp. 81–91, (Edited by A. J. Freeman and R. B. Frankel) Academic Press, New York (1967).
11. HAACKE G. and BEEGIE I. C., *J. Phys. Chem. Solids* **28**, 1699 (1967).
12. LOTGERING F. K., VAN STAPELE R. P. and VAN DER STEEN G. H. A. M. and VAN WIERINGEN J. S., *J. Phys. Chem. Solids* **30**, 799 (1969).
13. YOKOYAMA H. and CHIBA S., *J. phys. Soc. Japan* **27**, 505 (1969).
14. PLUMIER R. and LOTGERING F. K., *Solid State Commun.* **8**, 477 (1970).
15. BERGER S. B., BUDNICK J. I. and BURCH T. J., *Phys. Rev.* **179**, 272 (1969).
16. STAUSS G. H., *Phys. Rev.* **181**, 636 (1969).
17. POUND R. V., *Prog. nucl. Phys.* **2**, 21 (1952).
18. LEE K. and ANDERSON W. A., *Nuclear spins, moments, and magnetic resonance frequencies*, 1967, p. E-72, *Handbook of Chemistry and Physics*, 49th edition, 1968–1969 (The Chemical Rubber Co., Cleveland, Ohio).
19. SMIT J. and WIJN H. P. J., *Ferrites*, ch. III, Sec 10, (John Wiley and Sons, New York, 1959, Centrex, Eindhoven, 1959).
20. de GENNES P. G., PINCUS P. A., HARTMANN-BOUIRON F. and WINTER J. M., *Phys. Rev.* **129**, 1105 (1963).
21. HUANG N. L., ORBACH R., ŠIMÁNEK E., OWEN J. and TAYLOR D. R., *Phys. Rev.* **156**, 383 (1967).
22. HOLTON W. C., DE WIT M., WATTS R. K., ESTLE T. L. and SCHNEIDER J., *J. Phys. Chem. Solids* **30**, 963 (1969).
23. VAN STAPELE R. P. and LOTGERING F. K., to be published in *J. Phys. Chem. Solids*.
24. BLASSE G. and SCHIPPER D. J., *J. inorg. nucl. Chem.* **26**, 1467 (1964).

OSCILLATORY DEPENDENCE OF SUPERCONDUCTIVE CRITICAL TEMPERATURE ON NUMBER OF VALENCY ELECTRONS IN Cu₃Au-TYPE ALLOYS

E. E. HAVINGA, H. DAMSMA and M. H. VAN MAAREN

Philips Research Laboratories, N.V. Philips' Gloeilampfabrieken,
Eindhoven, Netherlands

(Received 6 January 1970)

Abstract—The superconducting critical temperature, the magnetic susceptibility and the thermo-electric power of a number of pseudo-binary *B₃A*-type alloys with Cu₃Au-structure have been investigated. An oscillatory dependence of the properties on the number of valence electrons per atom was observed. The constituents of the alloys were mainly non-transition metals: for the *A*-elements Ca, Y, La and Th and for the *B*-elements In, Sn, Tl and Pb. The results can be explained by taking into account the influence of the scattering of electrons by Bragg-planes near the Fermi surface on the electron density of states and on the superconductive interaction parameter. In addition 13 other Cu₃Au-type compounds with mainly non-transition metals have been prepared. The superconductivity of 19 out of the 25 Cu₃Au-type compounds investigated, can be fitted into the general scheme of oscillatory behaviour of *T_c* with *n*. The absence of superconductivity for 5 of the compounds can be ascribed to magnetic interactions.

1. INTRODUCTION

IN A PREVIOUS paper [1] it was shown that in the Cu₃Au-type alloy system LaTi₃–LaSn the superconductive critical temperature, *T_c*, follows a *W*-like curve if plotted as a function of the valency-electron concentration. Other properties, such as the room temperature value of the magnetic susceptibility and the thermo-electric power, *S*, were shown to be oscillatory as well. It was reported that similar behaviour was observed in several other alloy systems in this structure type. In this paper we present the experimental evidence that it is indeed a characteristic property of non-transition metal Cu₃Au-type alloys to show oscillatory *T_c*, *χ* and *S* vs. *n* curves, with maxima and minima at approximately fixed values of the electron concentration *n*. An explanation of these results, based on Brillouin-zone effects, will be discussed.

2. PREPARATION

All alloys were prepared by heating the elements in the appropriate amounts. The

starting materials had a purity of 99.9 per cent or better, the *B* metals being of grades

used. If the alloy to be prepared does not readily decompose on exposure to normal room conditions, the elements were melted together in an Argon arc, the mixture being remelted several times to approach homogeneity. If the X-ray diffraction pattern showed that the reaction was incomplete, the sample was given a further heat-treatment in an evacuated and sealed quartz vessel. In the list of the different systems investigated (Table I) this method is indicated by A, followed by the temperature in degrees centigrade and the duration of the annealing. The other method, used to prepare alloys that

Table 1. Survey of the Cu_3Au -type alloy system investigated

System	Preparation	Measured properties	Second phases present and remarks
$\text{La}(\text{In}_{1-x}\text{Sn}_x)_3$	A	T_c, χ, S (Fig. 2), $\chi(T)$ (Fig. 10)	—
$\text{La}(\text{Tl}_{1-x}\text{Sn}_x)_3$	Mo, 1750°	T_c, χ, S (Fig. 4)	for $x < 0.3$ traces of Tl
$\text{La}(\text{Tl}_{1-x}\text{Pb}_x)_3$	Mo, 1750°	T_c, S (Fig. 3)	(Pb, Tl), sometimes up to 15 per cent
$\text{La}(\text{Pb}_{1-x}\text{Sn}_x)_3$	Mo, 1750°	a, T_c, χ, S (Fig. 9)	—
$\text{Ca}(\text{Tl}_{1-x}\text{Pb}_x)_3$	Mo, 1750°	T_c (Fig. 8)	(Pb, Tl), sometimes up to 15 per cent
$\text{Y}(\text{In}_{1-x}\text{Sn}_x)_3$	Mo, 1600° (480°, 20 days)	T_c, S (Fig. 6)	InSn up to 5 per cent, for $x > 0.6$ unstable
$\text{Y}(\text{In}_{1-x}\text{Pb}_x)_3$	$x < 0.5$: A, else Mo 1750° (600°, 25 days)	T_c, χ, S (Fig. 5)	traces of Pb for $x > 0.7$
$\text{Th}(\text{In}_{1-x}\text{Sn}_x)_3$	$x < 0.6$: A (1000°, 10 days) $x > 0.6$: Mo, 1800° (400°, 10 days)	T_c (Fig. 7)	sometimes traces of In sometimes traces of Sn
$(\text{La}_{1-x}\text{Th}_x)\text{Sn}_3$	Mo, 1600° (450°, 30 days)	T_c, χ, S (Fig. 2)	—
$(\text{La}_{1-x}\text{Th}_x)\text{Pb}_3$	Mo, 1600° (1800°, 25 days, $x < 0.5$) (350°, 30 days, $x > 0.5$)	T_c, χ, S (Fig. 3)	traces of Pb for $x > 0.6$

Note: In all cases, except $\text{La}(\text{Pb}, \text{Sn})_3$, the lattice dimensions a are to be found in Fig. 1.

decompose at normal room conditions, involved heating the weighted elements for half an hour in an induction-heated furnace in evacuated and sealed Mo-vessels, well above the melting point of the alloy. This method is indicated in Table 1 by Mo, followed by the heating temperature in degrees centigrade, and by the temperature and duration of the annealing. The latter was always performed in the original and unopened Mo-vessel, covered by a sealed and evacuated quartz envelope.

In several systems we did not take the ideal ratio 1:3 for the elements forming the alloy AB_3 , but the ratio 1:2.9 instead. In these systems the normal ratio 1:3 gave rise to a large second phase content, the B -metal. This can be ascribed to the presence of some oxygen in the A metals leading to an excess of B in the reacted mixture. A few experiments showed that an even larger reduction of the B -content in the reaction mixture did not change the superconductive critical temperature by more than 0.1°K, though other second phases then appeared. This shows that in our systems the ratio of A elements to B elements is a relatively unimportant parameter as far as supercon-

ductivity is concerned, probably because of the narrow stability regions of the Cu_3Au -type compounds. Even with this variation in $A:B$ ratio we did not always succeed in preparing single-phase Cu_3Au -type alloys. For such samples the nature and relative abundance of the second phase present are also reported in Table 1.

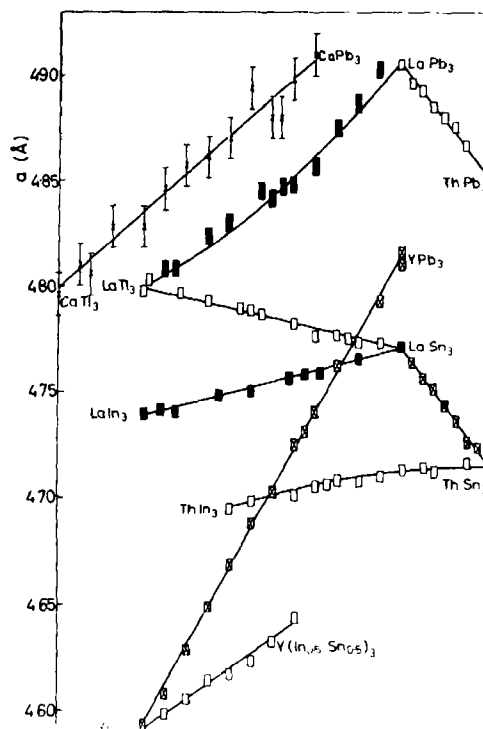
3. MEASURING METHODS

After preparation, the samples were crushed and a powder X-ray diffraction pattern measured. Those samples that had been prepared in sealed vessels were handled in a glove box, filled with dry nitrogen. Their X-ray patterns were obtained from powder in a special sample holder, which allowed it to stay in the inert atmosphere during exposure. Exposures were made on a Philips wide-range X-ray diffractometer PW 1050/30 in combination with an AMR X-ray focussing monochromator using $\text{CuK}\alpha$ radiation. If the difference in atomic number of the A and B -type atoms exceeded 20 per cent we always found superstructure lines of the Cu_3Au -structure in addition to the normal f.c.c. lines. The intensity of these lines increased with increasing difference in the scattering power

of the A and B -atoms in accordance with the calculated intensities of a completely ordered structure. Moreover, splat cooling of a few samples indicated that even such samples were completely ordered as inferred from the X-ray diagrams and substantiated by measuring an unchanged superconductive critical temperature. The invariance of the superconductivity at varying cooling rate during the preparation was also observed for some alloys where no superstructure lines could be observed because of the small difference in scattering power of the A and B atoms. The stability of the ordered structure is probably due to the rather large electronegativity difference between the A and B atoms in all of our alloys. In our opinion the evidence given above is sufficient to conclude that in all cases we have obtained the ordered Cu_3Au -type structure.

The unit cell dimension of each sample was determined and the results are plotted in Fig. 1. Although the accuracy is limited to about $\pm 0.0025 \text{ \AA}$ the results clearly show a very regular behaviour upon the various substitutions, showing that we have obtained real alloys and not mere mixtures. Moreover, higher accuracy of the cell dimensions was hardly obtainable for a number of samples, especially those containing Ca and Th, the width of the peaks being too large. For the Ca-compounds even this accuracy could not be achieved, but it is only about $\pm 0.01 \text{ \AA}$. In the system YIn_3 with substitution of Sn for In we found a solubility limit near 60 per cent Sn. This is in accordance with the reported non-existence of YSn_3 as a Cu_3Au -type compound[2].

Superconductivity was detected by measuring the change in the mutual inductance of a balanced pair of coils at 740 Hz. The temperature was measured by a carbon resistor, calibrated against the vapour pressure of liquid He and the transition of pure Pb. Temperatures below 1°K were obtained by adiabatic demagnetisation of KCr-alum, and superconductivity was observed by monitoring



the susceptibility of CeMg-nitrate single crystals. The lowest temperature reached was 0.05°K . We defined T_c as the midpoint of the curve of the susceptibility change. The width of the transitions, indicated by bars in the graphs of the next section, are the intersections of the tangent at T_c with the 0 and 100 per cent transition level. In most samples less than 5 per cent of the transition had taken place at temperature above the higher point of the bar and at the lower point of the bar 80 to 90 per cent of the transition was completed.

Room temperature magnetic susceptibilities,

χ , were measured by a standard Faraday method at about 9000 Oe. For a few samples the susceptibility was also measured over a wider temperature range. The thermoelectric power, S , was obtained by measuring the voltage over a thin, freshly cleaved sample placed between two silver electrodes at 25 and 40°C, respectively. Only samples showing metallic lustre gave reproducible results.

4. RESULTS

A survey of the various systems investigated is given in Table 1. Indicated are the preparation method, the numbers of the figures where the results of the different measurements are to be found, and the nature and amount of second phases, if present. In Figs. 2-9 the

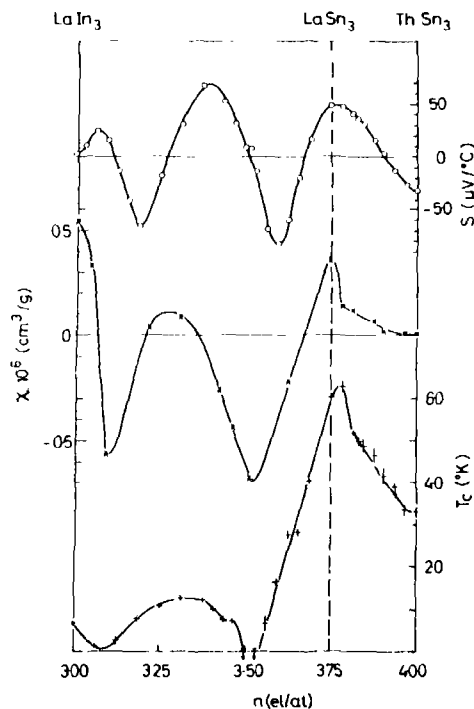


Fig. 2 Superconductive critical temperature T_c , room temperature magnetic susceptibility χ and thermoelectric power S of alloys $\text{La}(\text{In}_{1-x}\text{Sn}_x)_3$ and of alloys $(\text{La}_{1-x}\text{Th}_x)\text{Sn}_3$, plotted as a function of valency electron concentration n .

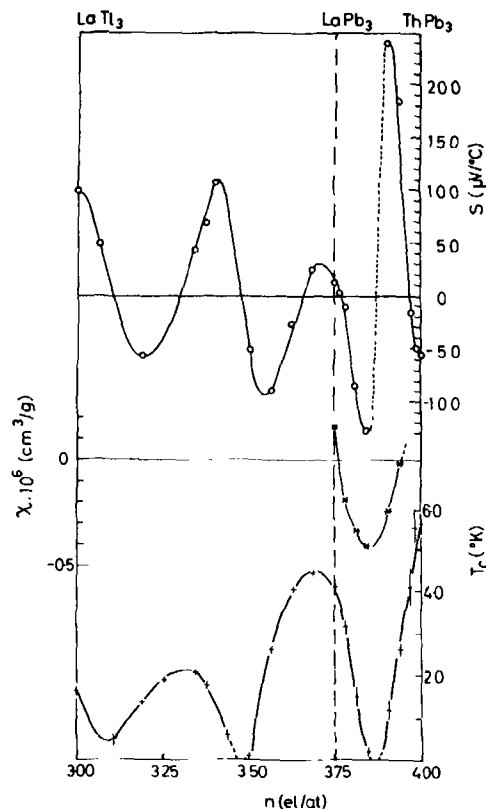
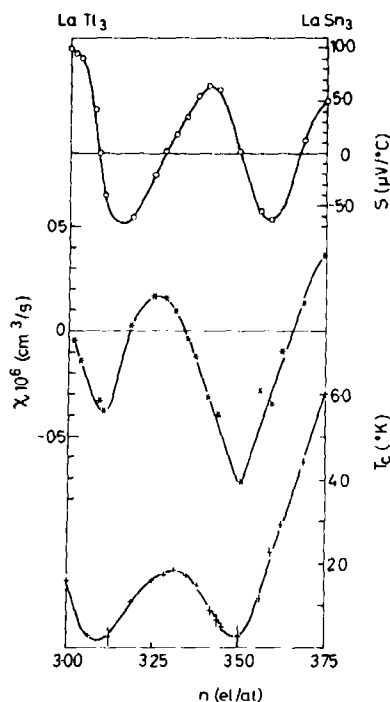
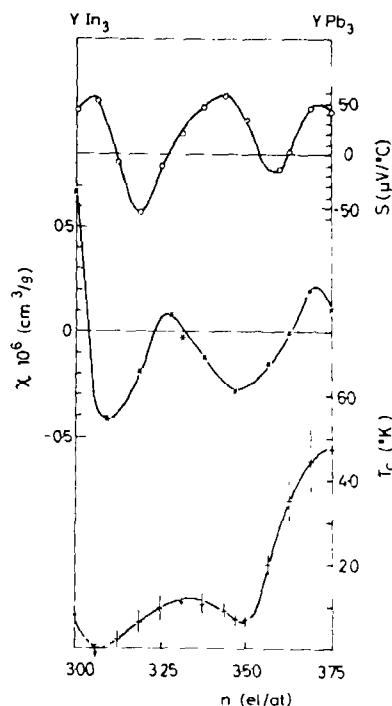


Fig. 3 T_c , χ and S of alloys $\text{La}(\text{Tl}_{1-x}\text{Pb}_x)_3$ and $(\text{La}_{1-x}\text{Th}_x)\text{Pb}_3$.

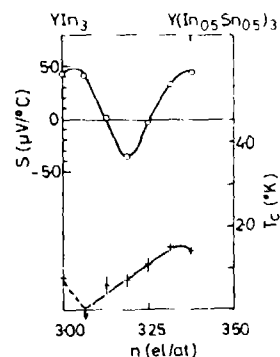
superconducting critical temperature T_c and, if measured, the room-temperature thermoelectric power, S , and the room-temperature magnetic susceptibility, χ , are plotted as a function of the composition. When the electron concentration n has varied with substitution, this parameter is indicated also. In Fig. 9 some χ vs. T curves, measured over the temperature range 77-500°K, are given. Finally, in Table 2 we summarised the superconducting critical temperatures and the unit cell dimensions of all binary alloys investigated. Included are also a number of alloys that are not part of the systems in the figures.

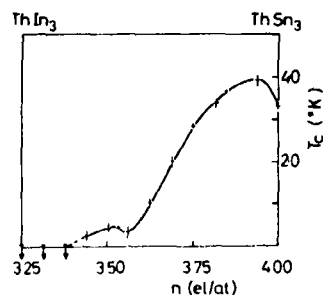
5. DISCUSSION

The results, presented in Figs. 2 and 3, show very clearly that the curves of the critical

Fig. 4. T_c , χ and S of alloys $\text{La}(\text{Ti}_{1-x}\text{Sn}_x)_3$.Fig. 5. T_c , χ and S of alloys $\text{Y}(\text{In}_{1-x}\text{Pb}_x)_3$.

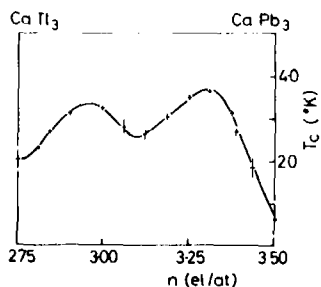
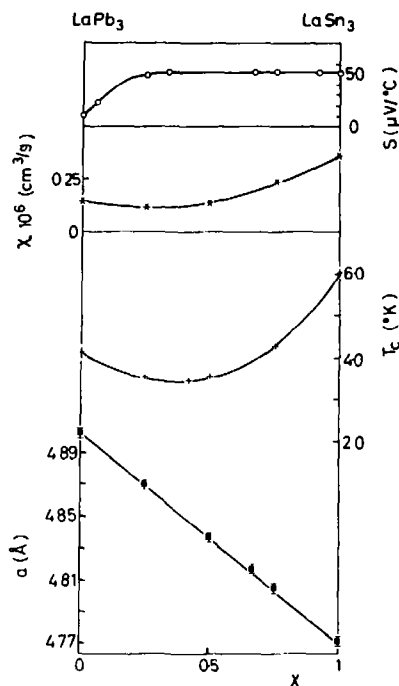
temperature vs. valency electron concentration are similar in most of the systems investigated. Although the values of the critical temperature T_c may be rather different at certain valency electron concentration, we find relative minima in the T_c at n -values around 3.1, 3.5 and 3.9, whilst maxima are found near n -values of 2.95, 3.3 and 3.7. The S vs. n and χ vs. n curves also show an oscillatory character, χ being in phase with the T_c and S about a quarter of a period out of phase. Two exceptions are found: in the system ThIn_3 - ThSn_3 the curve is still oscillatory, while in the system LaSn_3 - ThSn_3 the minimum at $n=3.9$ is missing. In low temperature X-ray diagrams we found some indications, that in the latter system the unit cell is slightly distorted towards a rhombohedron ($\alpha=89.3^\circ$), but due to the broadness of the peaks this interpretation is not beyond doubt. Such a deformation would, in the

Fig. 6. T_c and S of alloys $\text{Y}(\text{In}_{1-x}\text{Sn}_x)_3$.

Fig. 7. T_c of alloys $\text{Th}(\text{In}_{1-x}\text{Sn}_x)_3$.

tance, which may be seen for instance from a comparison of the systems LaIn_3 – LaSn_3 and LaTi_3 – LaSn_3 . The fact that the oscillatory curves are found in systems with very different kinds of atoms rules out the possibility that the striking effect is due to the special influence of lanthanum. Moreover, as Ca and even Na can replace La without essentially changing the oscillatory character of the T_c vs. n curves, it is clear that the alloys behave like non-transition metal alloys. From these observations we arrive at the conclusion that the oscillatory behaviour of the T_c vs. n , the χ vs. n and the S vs. n curve must be due to a general property of the Cu_3Au -type structure, and because of the non-transition metal character an explanation with the help of a nearly-free electron model will be appropriate.

An oscillatory T_c vs. n curve, though normal in transition metal systems, is rather new for a non-transition metal system. In most non-transition metal systems only a steady rise of T_c with n is observed, e.g. in several Pb alloys. In the PbTi -system T_c decreases very

Fig. 8. T_c of alloys $\text{Ca}(\text{Tl}_{1-x}\text{Pb}_x)_3$.Fig. 9. T_c , χ , S and lattice dimension a of alloys $\text{La}(\text{Pb}_{1-x}\text{Sn}_x)_3$.

rapidly with decreasing value of n near $n = 3.1$ [5], which could be explained in a satisfactory manner by Brillouin-zone effects [6]. However, a rise in T_c at lower n -values, which would be expected from this explanation, could not be observed because of a change of the structure from f.c.c. to hcp. A T_c decreasing with increasing valence electron concentration is found in the system InHg [7]. It was shown earlier [8] that this again can be explained if Brillouin-zone effects are taken into account. The only other oscillatory T_c vs. n curve measured so far is found in the metastable simple cubic Te – Au alloys [9]. Here also the thermoelectric power shows an irregular behaviour, and Brillouin-zone effects were shown to explain these results. The rather scanty information about Brillouin-zone effects as striking as in our systems is, however, not too surprising. Most non-transition metal-alloy systems have either

very simple structures, such as f.c.c. or hcp, which have only very few scattering Bragg-planes, or can be realised only at narrow ranges of the number of valence electrons per atoms. In the Cu_3Au -type structure we have, on the other hand, a not too simple structure type that can be realised for alloys over a large range of n -values.

We will show now that Brillouin zone effects indeed lead to such oscillatory T_c , S and χ vs. n curves. To that end we have plotted in Fig. 11(a) the well-known behaviour of the density of states, $N(E)$, as a function of energy for a nearly-free electron model. If the electrons were completely free the dotted curve would be followed. To illustrate the influence of the periodic lattice potential we assume that at energy M a form of Bragg planes would be attained. If these planes have a non-vanishing scattering power for the electrons, the Fermi sphere will bulge out upon approaching and the density of states will increase faster than for the free-electron model. Already at A the sphere will touch the planes, and at this point the derivative of $N(E)$ changes abruptly from $+\infty$ to a negative value because, starting from this value, parts of the phase-space are forbidden. At energy B the filling of a next zone starts, again with an abrupt change in the density-of-states curve. Finally, near energy D the first zone is completely filled. This latter effect is due to a cooperation of the different Bragg planes and hence this feature leading to the maximum in the density of states near C is absent in the density of states curve derived for the influence of a single Bragg-plane. It may be remarked that the curve of the density of states vs. the valency electron concentration will be of a similar shape, because the energy in the free electron model is related to n as $n = \text{const. } E^{3/2}$, and the only influence of the Bragg planes is to expand the n -scale with respect to the $E^{3/2}$ -scale in the regions where N exceeds its free-electron value (near A) and to contract it at energies where N is smaller (near B and D).

The influence of the Bragg planes on the superconductive transition temperature can be found straightforwardly with the help of the consideration given in an earlier paper [6]. There it was stated that, although all electrons at the Fermi surface contribute to the interaction V which causes superconductivity, electrons in mixed O.P.W.'s are far more effective than electrons in single O.P.W.'s. The arguments, based on pseudo-potential theory are as follows. V is proportional to the averaged square of the matrix elements $M(\mathbf{k}, \mathbf{k} + \mathbf{q})$ that determine the scattering of an electron out of an O.P.W. $\mathbf{k}$ into an O.P.W. $\mathbf{k} + \mathbf{q}$. In the pseudo-potential theory M is approximated by the product of the structure factor $S(\mathbf{q})$ and a form factor $U(q)$. For non-transition metals the $U(q)$ vs. q curves are similar to each other, all having large values of $|U|$ only at small q -values. This means that electrons in single O.P.W.'s will be nearly exclusively scattered over small angles in the extended zone scheme, because only then is q small. On the other hand, in mixed O.P.W.'s the scattering

to an electron in a mixed O.P.W. $\mathbf{k}$ can be of large angle. Hence, in mixed O.P.W.'s we find those electrons in mixed O.P.W.'s mainly near A , at the right-hand side near B and at the left-hand side near D . Hence the superconductive interaction parameter I will depend on E as sketched in Fig. 11(b). The superconductive critical temperature, given by the BCS (strong-coupling) formula

$$T_c = 1.14 \theta \exp\left(-\frac{1 + \frac{1}{2} \frac{N(E_F)}{N(E_F - \epsilon_F)}}{\frac{1}{2} \frac{N(E_F)}{N(E_F - \epsilon_F)}}\right),$$

will show the behaviour sketched in Fig. 11(c).

For the thermo-electric power at room temperature, S , we again have two effects

to take into account. In the first place we have the influence of the deformation of the Fermi surface and secondly that of the much increased probability of large-angle scattering near A and C . We use the general formula

$$S = \pi^2 k^2 \frac{T}{3e} \cdot \left(\partial \ln \frac{\sigma(E)}{\partial E} \right)_{E=E_F} \quad [11],$$

where $\sigma(E)$ is the energy-dependent electrical conductivity, E_F the Fermi energy and e the -negative- value of the charge of the electron. The influence of the increased largeangle scattering is to decrease the conductivity and hence this effect alone would give an S vs. E curve as sketched in Fig. 11(d), labelled U -processes. On the other hand we can calculate the influence of the Brillouin-zone effects proper, under the assumption that the relaxation time τ is not changed, using the general formula for the conductivity

$$\sigma = \frac{e^2 \tau}{4\pi^2 \hbar} \int v \cdot dF \quad [10],$$

where F denotes the Fermi area and v the Fermi velocity. The curve labelled $F.S.$ in Fig. 11(d) gives the results for a nearly-free electron model. If we compare both curves of Fig. 11(d) with the experimental S vs. n curves, we see that these experimental curves are very much like the calculated curve labelled U -processes. Hence the increased largeangle scattering is the dominant effect on S , which gives support for its influence on T , also.

In one system, $\text{LaPb}_{1-x}\text{ThPb}_x$, we do find an S vs. n curve that is similar to part of the calculated $F.S.$ -curve, but in the reverse n (or E)-direction. Such a curve is to be expected if we start with a number of electron surfaces in one of the higher zones instead of with a single electron sphere. At a concentration n where the surfaces touch, their contribution to the thermoelectric power S changes abruptly from negative to positive. Namely, at lower n -values the Fermi surface area

increases with increasing Fermi energy, but when necks between the various surfaces are formed the Fermi surface shrinks rapidly with increasing Fermi energy.

For a large number of alloys the magnetic susceptibility χ is negative. In these diamagnetic regions, the χ vs. n curves closely resemble those found for various In- and Bi-alloys [11], and even the temperature dependences of χ are similar. Hence the explanation proposed for the In- and Bi-alloys [11] may also be appropriate for our systems. For simple bands the diamagnetic susceptibility may be calculated in the Landau-Peierls approximation. If because of Brillouin-zone effects two bands are present at the Fermi surface, this approximation breaks down due to a neglect of non-diagonal terms. Adams showed, that in such configurations the diamagnetic contribution is much increased over the L.P.-value [12]. A sketch of the expected behaviour is shown in the lower dotted curve of Fig. 11(e). In addition to the diamagnetic susceptibility, the paramagnetic contributions of the spins of the electrons must also be taken into account. For simple bands the Pauli approximation may be used. This leads to a χ -value proportional to $N(E)$, three times larger than the -absolute- value of the Landau-Peierls susceptibility. In narrow bands this contribution may be enlarged because of the spin enhancement effect. In the upper dotted curve of Fig. 11(e) we have sketched the expected behaviour. It is seen from the continuous curve in Fig. 11(e), which indicates the resulting total magnetic susceptibility, that a χ vs. E curve can be obtained that closely resembles the observed χ vs. n curves.

It may be remarked that in Fig. 11 only the point M , where the Fermi surface of a free-electron model just touches the form of Bragg planes, is fixed by the simple theory. The energies of the other points depend on the magnitude of the interactions between the electrons and the Bragg plane. In the Cu_3Au structure, which is simple cubic, points com-

parable with M are expected to be found at $n = 2.97$ and $n = 3.90$, where the forms $\{201\}$ and $\{211\}$ are met, respectively. It is gratifying that the experimental curves around these n -values closely resemble the curves sketched in Fig. 11, which substantiates the given explanation.

With the knowledge of this general behaviour of T_c with the valence electron concentration n , the data obtained for binary compounds (Table 2) is readily explained. Since maxima are found near $n = 3.75$ and $n = 4.00$ in the T_c vs. n curves, alloys with these concentrations of electrons are expected to become superconducting at relatively high

critical temperatures. On the other hand alloys with $n = 3.50$ are situated near a minimum in the T_c vs. n curves and will have low T_c -values. Alloys with n -values of 2.75, 3.00 or 3.25 are neither in minima nor maxima and hence will have intermediate T_c -values. Of course, these rules are only approximate because the T_c -values in the various systems differ appreciably as a consequence of the different strength of the interaction with the Bragg planes. Nevertheless it is seen from the experimental data of Table 2 that the rule is followed. Exceptions are ThIn_3 , which was already mentioned to be part of an irregular system ThIn_3 - ThSn_3 , and further UAl_3 , UIn_3 ,

Table 2. Superconductive critical temperatures T_c and unit cell dimensions a of binary Cu_3Au -type compounds, containing three non-transition metal atoms per cell

Compound	n	T_c (°K) and width	T_c (°K) lit.	a (Å)	a_{int} (Å), Ref (if empty, [2])
NaPb_3	3.25	5.62 ± 0.09	2.0 [11]	4.888	4.884
CaTi_3	2.75	2.04 ± 0.21		4.796	4.803
CaPb_3	3.50	0.65 ± 0.40			
SiBi_3	4.25	5.70 ± 0.08			
YIn_3	3.00	0.78 ± 0.21			
YTi_3	3.00	1.52 ± 0.10			
YPb_3	3.75	4.72 ± 0.09			
LaIn_3	3.00	0.70 ± 0.04			
LaTi_3	3.75	1.63 ± 0.04			
LaPb_3	3.75	4.10 ± 0.02			
LaSn_3	3.75	6.02 ± 0.08			
YbAl_3	2.75	0.94 ± 0.15			
YbIn_3	2.75 [*]	0.05			
YbPb_3	3.50	0.23 ± 0.10		4.833	4.862 [12]
LuGa_3	3.00	2.30 ± 0.11	5.69 [12]	4.191	4.169
LuIn_3	3.00	0.24 ± 0.14		4.547	4.544
ThIn_3	3.25	0.05		4.694	4.695
ThTi_3	3.25	0.87 ± 0.03		4.748	4.748
ThPb_3	4.00	5.55 ± 0.30		4.853	4.855
ThSn_3	4.00	3.33 ± 0.08		4.714	4.718
ZrHg_3	2.50	3.28 ± 0.30		4.368	4.3652
UAl_3	?	0.07		4.266	4.287
UIn_3	?	0.07		4.595	4.6013
CeIn_3	?	0.07		4.687	4.688
CeSn_3	?	0.07		4.717	4.721
* BaBi_3	4.25	5.80 ± 0.20		$a = 5.19$ $c = 5.16$	$a = 5.188$ $c = 5.157$
* SrPb_3	3.50	1.85 ± 0.08		$a = 4.962$ $c = 5.025$	$a = 4.965$ $c = 5.035$

* Alloys with CuTi_3 structure (Slightly deformed Cu_3Au -type)

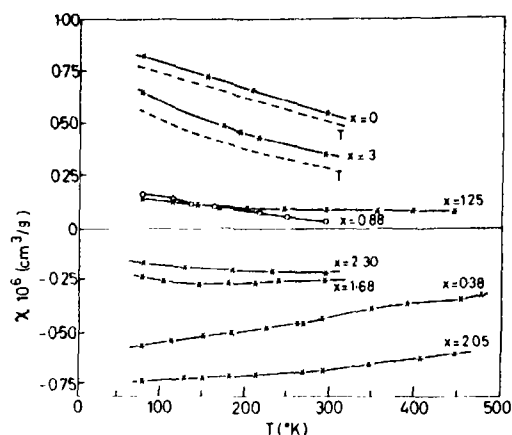


Fig. 10. Dependence of the magnetic susceptibility on temperature for several alloys $\text{La}(\text{In}_{1-x}\text{Sn}_x)_3$. The curves marked T are calculated from the plots of χ^{-1} (corrected) vs T of Ref. [4].

CeIn_3 and CeSn_3 . In the latter compounds the value of the magnetic susceptibility points to the presence of magnetic moments, that are known to be destructive for the occurrence

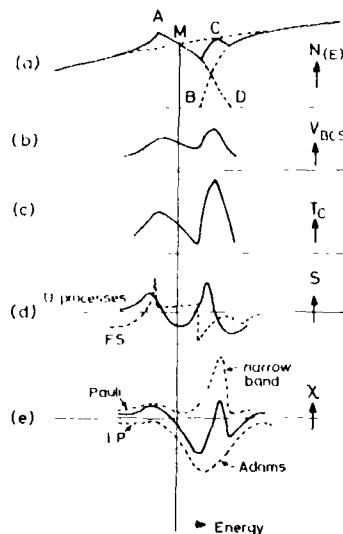


Fig. 11. Expected Brillouin-zone effects on (a) density of states $N(E)$, (b) superconductive interaction parameter V , (c) superconductive critical temperature T_c , (d) thermo-electric power S , and (e) magnetic susceptibility χ .

of superconductivity. The data further suggest a new maximum in the T_c vs. n curves near $n = 4.25$. However, we have not yet succeeded in preparing alloys in the range $4.00 < n < 4.25$. The superconductivity of some Yb compounds points strongly to divalent Yb, because the magnetic moment of Yb^{3+} certainly would destroy superconductivity, as probably is the case in YbIn_3 . It may be remarked that this is the first occasion where an Yb compound has been found to become superconductive. Finally we have included in Table 2 two superconducting compounds with the CuTi_3 -structure. This structure is an only slightly tetragonally deformed Cu_3Au -structure. It is seen that this deformation has little or no influence if the T_c is high, (BaBi_3 and SrBi_3), whilst for T_c near a minimum the deformation tends to raise T_c because of a blurring of the Brillouin zone effects (CaPb_3 and SrPb_3).

Acknowledgements—Thanks are due to Mr P. Hokkeling, who carried out the first stages of the preparations and to Mr J. M. Kamis for his cooperation in the T_c measurements below 1.2°K.

REFERENCES

1. HAVINGA F. F., *Phys. Lett.* **28A**, 350 (1968).
2. PEARSON W. B., *Handbook of Lattice Spacings and Structures of Metals and Alloys*, Vol. 2, Pergamon Press Oxford (1967).
3. GAMBINO R. J., STEMPLE N. R. and FOXEN A. M., *J. Phys. Chem. Solids* **29**, 295 (1968).
4. FOXEN A. M. and GAMBINO R. J., *Phys. Lett.* **28A**, 214 (1968).
5. CLEASON T., *Phys. Rev.* **147**, 340 (1966).
6. HAVINGA F. F., *Phys. Lett.* **26A**, 244 (1968).
7. MERRIAM M. F., JENSEN M. A. and COLLES B. R., *Phys. Rev.* **130**, 1719 (1963).
8. HAVINGA F. F., *11th Int. Conf. on Low Temperature Physics*, Vol. 2, p. 756, St. Andrews (1968).
9. ISUFI C. C. and NEWKIRK I. R., *Phys. Rev.* **183**, 619 (1969).
10. ZIMAN J. M., *Principles of the Theory of Solids*, pp. 183, 202, Cambridge University Press, Cambridge (1965).
11. VERKIN B. I., SVECHKAREV I. V. and KUZ'NICHENKO I. B., *Soviet Phys. JETP* **23**, 954 (1966).
12. ADAMS H. F. N., *Phys. Rev.* **89**, 633 (1953).
13. MATTHIAS B. T. and HULM J. K., *Phys. Rev.* **87**, 799 (1952).
14. VAN VUCHT J. H. N. and BUSCHOW K. H. J., *Philips Res. Rep.* **19**, 319 (1964).
15. PALENZONA A., *J. less-common Metals* **10**, 290 (1966).

A CALCULATION OF THE CONTRIBUTION OF QUASIPARTICLE ANISOTROPY TO THE ISOTROPIC KNIGHT SHIFT

R. A. CRAIG*

Department of Physics, University of California at Riverside, Riverside, Calif. 92507, U.S.A.

(Received 12 November 1969; in revised form 5 January 1970)

Abstract—A model Fermi liquid-type calculation is performed to determine the contribution of anisotropy in the quasiparticle-quasiparticle interaction to the isotropic Knight shift. For reasonable values of the parameters of the theory, good agreement with the observed behavior of the Knight shift for small values of impurity concentration is obtained.

1. INTRODUCTION

THATCHER and Hewitt[1] have reported a dip in the low temperature value of the isotropic Knight shift of indium for low concentrations of impurities bordering on indium in the periodic table (i.e. Cd, Sn, Hg, Tl, Pb). Differences between the various solutes lie primarily in the rates with which the Knight shift decreases with concentration; when plotted vs. residual resistivity, the points for various solutes appear to lie on a common curve (Fig. 1). Measurements of the specific heat of In-Sn alloys[2] show no similar dip so that the phenomena cannot be ascribed to anomalous behavior in the density of electronic states.

One other physical phenomenon shows a similar dip for low concentrations of impurities—the superconducting transition temperature. This behavior of the transition temperature has been satisfactorily explained[3] on the basis of a combination of a linear 'valence' effect which depends on the type of solute involved and is important for larger values of the solute concentration and a mean free path effect which dominates for smaller values of impurity concentration. In superconductivity, the mean free path effect is explained as the removal of the contribution from the aniso-

tropy of the phonon modulated electron-electron interaction. The phonon induced inter-electron interaction is clearly not the explanation of the dip in the Knight shift. Prange and Sachs[4] have shown that in the Landau theory extended to include phonons, the susceptibility is unaffected by the phonons, provided that the electron-phonon interaction is diagonal in electronic spin. We assume this to be

anisotropic. In Section 2 we derive the quasiparticle interaction vertex χ_{ij} . In Section 3 we analyze the results of this calculation and its connection with the experimental situation. In Section 4 we summarize the conclusions that can be inferred from this work.

2. DERIVATION OF ANISOTROPY CONTRIBUTION

The Knight shift is the shift in nuclear Zeeman energy introduced by placing the atom in question in the presence of a paramagnetic electron gas[6]; it is explained by the fact that the metallic electrons which interact with the nuclear spin via the contact interaction have a

*Present address: Department of Physics, Oregon State University, Corvallis, Oregon 97331, U.S.A.

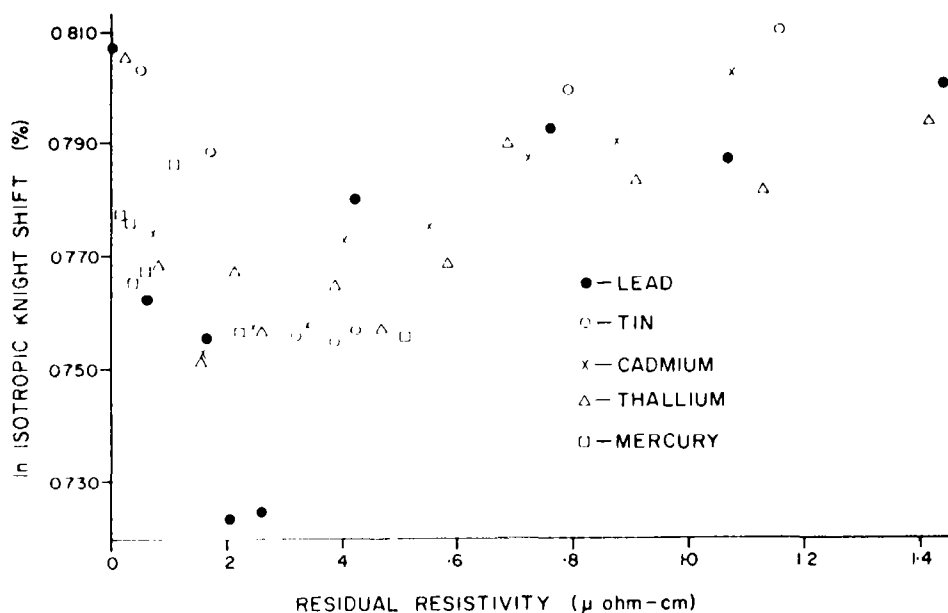


Fig. 1.

net polarization because of the presence of the magnetic field. Experimentally, this appears equivalent to an additional magnetic field and the pertinent quantity is $(h - 1)$

$$K = \frac{\Delta H}{H_0} = \frac{8\pi}{3} \gamma_e \left| \sum_{\mathbf{k}, \sigma} |\psi_{\mathbf{k}, \sigma}(0)|^2 \frac{\sigma_z n_{\sigma}(\mathbf{k})}{H_0} \right|. \quad (1)$$

In equation (1), $\psi_{\mathbf{k}}(0)$ is the electronic wavefunction of wavevector $\mathbf{k}$ (we use the extended zone scheme) and spin σ at an ionic site, $n_{\sigma}(\mathbf{k})$ is the number of electrons of wavevector $\mathbf{k}$ and spin σ , γ_e is twice the Bohr magneton, and H_0 is the applied magnetic field. We shall assume that, to linear order in the magnetic field, the electronic wavefunction does not depend on spin. Then

$$K = -\frac{4\pi}{3} \gamma_e \sum_{\mathbf{k}_f} |\psi_{\mathbf{k}_f}(0)|^2 [\delta n(\mathbf{k}_f) - \delta n^*(\mathbf{k}_f)] \quad (2)$$

where we have written $n_{\sigma}(\mathbf{k}) = n_{\sigma}^0(\mathbf{k}) + \delta n_{\sigma}(\mathbf{k})$; we have restricted the wavevector to $\mathbf{k}_f$ as $\delta n_{\sigma}(\mathbf{k})$ is non-zero only for wavevectors lying on the Fermi surface. The bracketed term in (2) is directly related to the paramagnetic susceptibility of electrons of wavevector $\mathbf{k}_f$.

To calculate the contribution of the anisotropy of the quasiparticle-quasiparticle interaction to the expression in (2), we use the Landau Fermi liquid model suitably extended to include band structure effects [7-11]. In this model, the change in system energy induced by a disturbance is

$$\delta \epsilon = \sum_{\mathbf{k}, \sigma} E_{\sigma}^0(\mathbf{k}) \delta n_{\sigma}(\mathbf{k}) + \frac{1}{2} \sum_{\mathbf{k}, \mathbf{k}'} f(\mathbf{k}, \sigma; \mathbf{k}', \sigma') \delta n_{\sigma}(\mathbf{k}) \delta n_{\sigma'}(\mathbf{k}') \quad (3)$$

where $E_{\sigma}^0(\mathbf{k})$ is the electronic quasiparticle energy in the absence of the disturbance, $f(\mathbf{k}, \sigma; \mathbf{k}', \sigma')$ is the interquasiparticle inter-

action, and $\delta n_\sigma(\mathbf{k})$ is the change in $n_\sigma(\mathbf{k})$ induced by the disturbance. The energy of a quasiparticle in the presence of the disturbance is then

$$E_\sigma(\mathbf{k}) = E_{\sigma^0}(\mathbf{k}) + \sum_{\mathbf{k}', \sigma'} f(\mathbf{k}, \sigma; \mathbf{k}', \sigma') \delta n_{\sigma'}(\mathbf{k}'). \quad (4)$$

Consequently, the change in energy of a quasiparticle due to the applied magnetic field is

$$\delta E_\sigma(\mathbf{k}) = \gamma_\sigma \boldsymbol{\sigma} \cdot \mathbf{H}^0 + \sum_{\mathbf{k}', \sigma'} f(\mathbf{k}, \sigma; \mathbf{k}', \sigma') \delta n_{\sigma'}(\mathbf{k}'). \quad (5)$$

We write $\delta E_\sigma(\mathbf{k}) = \xi(\hat{\mathbf{k}}_F) \boldsymbol{\sigma} \cdot \mathbf{H}$ and split the quasiparticle interaction into a direct and an exchange part $f = f^0 + f^e \delta_{\sigma\sigma'}$, so that equation (5) becomes

$$\xi(\hat{\mathbf{k}}_F) = \gamma_e \int d\Omega \hat{h}_F N(\hat{\mathbf{k}}'_F) \times f^e(\hat{\mathbf{k}}_F, \hat{\mathbf{k}}'_F) \quad (6)$$

where $N(\mathbf{k}'_F)$ is the density of states of electrons at the Fermi surface and the integral is carried over the Fermi surface. Following the logic of Markowitz and Kadanoff, we insert the anisotropy of the quasiparticle-quasiparticle interaction by assuming $f^e(\mathbf{k}_F, \mathbf{k}'_F)$ to be separable

$$f^e(\hat{\mathbf{k}}_F, \hat{\mathbf{k}}'_F) = (1 + a(\hat{\mathbf{k}}_F)) f^e(1 + a(\hat{\mathbf{k}}'_F)) \quad (7)$$

with the angular average of the anisotropy $a(\hat{\mathbf{k}}_F)$ vanishing. Then equation (6) can be solved for $\xi(\hat{\mathbf{k}}_F)$ giving

$$\xi(\hat{\mathbf{k}}_F) = \gamma_e \left[1 - \frac{N f^e(1 + a(\hat{\mathbf{k}}_F)) \langle (1 + a) \rangle}{1 + N f^e \langle (1 + a)^2 \rangle} \right] \quad (8)$$

where we define

$$N(\cdots) = \int d\Omega_{\hat{\mathbf{k}}_F} N(\hat{\mathbf{k}}_F)(\cdots). \quad (9)$$

Thus the change in electronic quasi-

particle density induced by the magnetic field becomes

$$\delta n_\sigma(\mathbf{k}_F) = -\delta(E^\sigma(\mathbf{k}) - \mu) \times N(\mathbf{k}_F) \xi(\mathbf{k}_F) \boldsymbol{\sigma} \cdot \mathbf{H}^0 \quad (10)$$

so that the Knight shift is given by

$$K = \frac{4\pi}{3} \gamma_e \sum_{\mathbf{k}_F} N(\mathbf{k}_F) \xi(\mathbf{k}_F) |\Psi_{\mathbf{k}_F}(0)|^2 = \frac{4\pi}{3} \gamma_e^2 N \left\langle |\Psi_{\mathbf{k}_F}(0)|^2 \times \left(1 - \frac{N f^e(1 + a) \langle (1 + a) \rangle}{1 + N f^e \langle (1 + a)^2 \rangle} \right) \right\rangle. \quad (11)$$

There are, in this expression for the Knight shift, three anisotropy contributions: the anisotropy of the interquasiparticle interaction (included in $a(\hat{\mathbf{k}}_F)$), the anisotropy of $|\Psi_{\mathbf{k}_F}(0)|^2$ and the anisotropy of the density of states $N(\hat{\mathbf{k}}_F)$. We write

$$N(\hat{\mathbf{k}}_F) = N(1 + b(\hat{\mathbf{k}}_F)) \quad (12a)$$

and

$$K = \frac{4\pi}{3} \gamma_e^2 \frac{N \langle |\Psi_{\mathbf{k}_F}(0)|^2 \rangle_{av}}{1 + N f^e} \times \left\{ 1 + \langle bc \rangle_{av} + N f^e [\langle a^2 \rangle_{av} - \langle ac \rangle_{av}] - \frac{N f^e}{1 + N f^e} [\langle a^2 \rangle_{av} + 2 \langle ab \rangle_{av}] \right\} \quad (13)$$

Unlike the case of the superconducting transition temperature, the contribution of the anisotropy of the quasiparticle-quasiparticle interaction does involve the anisotropy of the density of states and of the electronic density at the nucleus. To proceed any further

in a straightforward manner would require detailed information on the anisotropy in all three of these quantities; such information is not available and we can at best make estimates of the magnitude of the effect of anisotropy in the quasiparticle-quasiparticle interaction. This we do in the following section.

3. ANALYSIS OF THE THEORETICAL RESULTS

We have calculated the Knight shift when the interquasiparticle interaction is anisotropic. The introduction of small amounts of impurities does not remove the anisotropy in the inter-quasiparticle interaction; instead it simply removes some of the effects of this anisotropy. If a quasiparticle scatters against an impurity, most of the information regarding the angular dependence of the preceding quasiparticle-quasiparticle collision is lost.* The principal contribution to the Knight shift from the anisotropy in the interaction between quasiparticles is that involving the quantity $(a^2)_{av}$ which enters through the angular correlation between successive quasiparticle scattering events. Thus the change in Knight shift expected when we introduce impurities to the point where all memory of angular correlations is lost between quasiparticle collisions is

$$\frac{\Delta K}{K} = \frac{(a^2)_{av} (Nf^e)^2}{1 + Nf^e} \quad (14)$$

A first guess at a characteristic value of Nf^e would be on the order of $-1/2$ Markowitz and Kadanoff, in their consideration of the contribution of anisotropy in the phonon moderated electron-electron interaction to the superconducting transition found $(a^2)_{av}$ to be of the order of magnitude of 0.01. If lacking any better figures, we use these, we

find the net contribution of the anisotropy of the quasiparticle-quasiparticle interaction would be positive and adding about 0.5 per cent. This is of the correct sign and barely an order of magnitude too small. We can do somewhat better than this, however, as we see that both the fractional anisotropy contribution to the Knight shift and the Knight shift itself are scaled by the factor $1/(1 + Nf^e)$. The scaling factor in the case of the Knight shift represents the exchange enhancement of the spin paramagnetism; for lithium [4]

$$\frac{\chi_s^{\text{expt}}}{\chi_s^{\text{free}}} = \frac{1}{1 + Nf^e} \cong 1.54 \quad (15)$$

where χ_s^{free} is the pauli spin paramagnetism for free electrons in lithium with the appropriate band mass and χ_s^{expt} is the measured value. The electronic specific heat constants γ of indium and lithium are nearly equal [12]; consequently, $\chi_{s,\text{Li}}^{\text{free}}$ and $\chi_{s,\text{In}}^{\text{free}}$ should also be nearly equal.* If we had a value of χ_s^{expt} for indium then we could determine the quantity Nf^e directly; measurements of χ_s^{expt} are extremely difficult, however, and these have not been done for indium. The Knight shift data is available for both these metals; the Knight shifts of Li and In are, respectively, 0.0249 and 0.81 per cent [1, 15, 16]. If we ignore the variation of the spin susceptibility with wave-vector the Knight shift is approximately [6]

$$K = \frac{8\pi}{3} \langle |\Psi_{\mathbf{k},\sigma}(0)|^2 \rangle_{av} \chi_s \quad (16)$$

*If the specific heats of indium and lithium were exactly equal, it would not necessarily follow that $\chi_{\text{Li}}^{\text{free}}$ was equal to $\chi_{\text{In}}^{\text{free}}$ —phonon interactions are important in determining the specific heat but make no contribution to the susceptibility. Calculations of this phonon enhancement [13–14] have been done for a number of metals including lithium, aluminum, and lead. Using these calculations we find

$$1.14\chi_{\text{Li}}^{\text{free}} \cong 1.49\chi_{\text{Al}}^{\text{free}} \cong 2.05\chi_{\text{Pb}}^{\text{free}}$$

*Quasiparticle collisions by definition are quite rare. Only a very small density of impurities is therefore required to guarantee that a quasiparticle will scatter against an impurity before interacting with another quasiparticle.

so that we can expect that $\chi_{\text{Li}}^{\text{free}} = \alpha\chi_{\text{In}}^{\text{free}}$ where α is a constant of order $\frac{1}{2}$ to 1. We shall inquire no further into this point as it does not affect the following argument indeed only serving to magnify the discrepancy between the Knight shifts of lithium and indium.

Were we to take the fermi electronic density at the nucleus to be the same for lithium we should get a value of 0.98 for Nf^e . In view of the fact that the electronic densities are almost certainly not the same, we should not take this figure seriously. It does seem reasonable, however, to expect that the entire factor of about 33 difference between the lithium and indium Knight shifts cannot be explained by the difference in wave function at the nucleus and that some of this factor can be attributed to a larger exchange enhancement in indium. In Fig. 2 we plot the locus of values of $(a^2)_{av}$ and Nf^e giving the experimental result of $\Delta K/K = 0.065$. This model calculation of the anisotropy contribution to the Knight shift is seen to give reasonable agreement with the experimental value of the impurity dip for sensible values of the parameters of the theory.

If on the other hand, we consider the specific heat, applying the same logic we have used here, we find the specific heat to be independent of the inter-quasiparticle interaction and consequently of its anisotropy. This follows in exactly the same manner as for the normal fermi liquid; the interaction

contributes terms to the specific heat which vanish as T^3 for low temperatures. In the ordinary, normal fermi liquid, the quasiparticle-quasiparticle interaction contributes to the density of quasiparticle states which can, in that case, be calculated. Here, the density of states is regarded as empirically determined. It is clear from the experimental evidence on the specific heat that the anisotropy in the inter-quasiparticle interaction makes no significant contribution to the density of states.

4. CONCLUSIONS

What have we done? We have calculated the contribution of the anisotropy of the electronic quasiparticle interaction to the Knight shift within the confines of a Landau fermi liquid model. The introduction of impurities, which cannot be included within this simple model* will remove the effects of this anisotropy because quasiparticles scattered by impurities between quasiparticle-quasi-

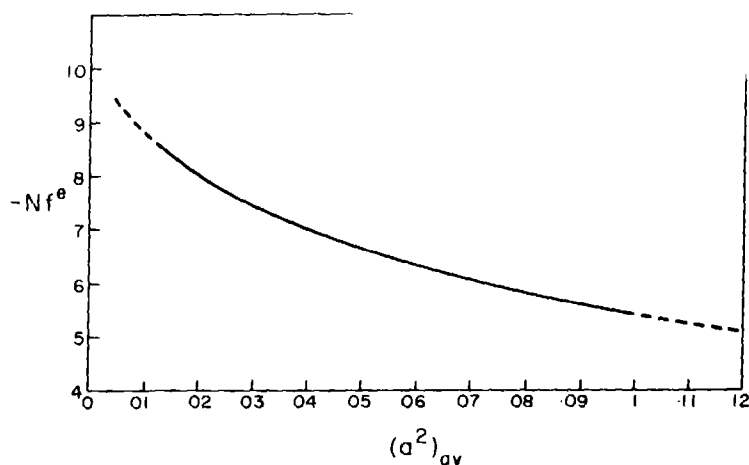


Fig. 2.

particle collisions lose the memory of the angular nature of the collisions. For reasonable values of the parameters of the theory, we find the anisotropy contribution to the Knight shift to be of the proper sign and of the proper order of magnitude to explain the experimental dip. In this regard, a caution must be made. This interpretation of the impurity dip is extremely sensitive to the value of the parameter Nf^e ; if this quantity is very small in magnitude, then the anisotropy in the interquasi particle interaction is not the explanation of this phenomenon. Calculations of $\langle |\psi_{kf}(0)|^2 \rangle_{av}$ for indium have been made which yield a value about fifty times greater than that for lithium[17]. These calculations give excellent agreement with the experimental Knight shift with no exchange enhancement. This agreement is very likely fortuitous; band structure calculations just barely give accurate results for the energies; the wavefunctions evolving from such calculations are far from accurate. It is also a bit difficult to believe that the fermi surface electrons of indium will, on the average, have fifty times the s wave character of that for lithium.

One last point is worthy of note; the principal effect of increasing the temperature will be to introduce collisions with thermal phonons. These phonon collisions should have the same randomizing effect as those associated with impurities. Consequently, no additional dip in the Knight shift should be observed by adding low concentrations of

impurities if the measurements are made at elevated temperatures.

Acknowledgements—The author wishes to thank Professors R. R. Hewitt and F. C. Thatcher and Mr. M. Daugherty for many helpful and informative discussions.

REFERENCES

1. THATCHER F. C. and HEWITT R. R. (To be published)
2. WHITE H. H. and MCCOLLUM D. C., *Bull. Am. phys. Soc.* **13**, 1671 (1968).
3. MARKOWITZ D. and KADANOFF L. P., *Phys. Rev.* **131**, 563 (1963).
4. PRANGE R. F. and SACHS A., *Phys. Rev.* **155**, 672 (1967).
5. PINES D., *Elementary Excitations in Solids*, p. 61 Benjamin, New York (1963).
6. SLICHTER C. P., *Principles of Magnetic Resonance with Examples from Solid State Physics* Harper and Row, New York (1963).
7. LANDAU L., *Zh. eks. teor. Fiz.* **30**, 1058 (1956); English transl. *Soviet Phys. JETP* **3**, 920 (1957).
8. LANDAU L., *Zh. eks. teor. Fiz.* **32**, 59 (1957); English transl. *Soviet Phys. JETP* **5**, 101 (1957).
9. LANDAU L., *Zh. eks. teor. Fiz.* **35**, 97 (1958); English transl. *Soviet Phys. JETP* **8**, 70 (1958).
10. ABRIKOSOV A. A. and KHLATNIKOV I. M., *Rep. Prog. Phys.* **22**, 329 (1959); *Usp. fiz. Nauk.* **66**, 177 (1958); English transl. *Soviet Phys. Usp.* **1**, 68 (1958).
11. JONES B. L. and McCURE J. W., *Phys. Rev.* **143**, 133 (1966).
12. KITTEL C., *Introduction to Solid State Physics*, 3rd Edn, p. 212 Wiley, New York (1967).
13. ANIMALU A. O. E., BONSIGNORI F., and BARTOLINI V., *Nuovo Cim.* **B42** 83 (1966).
14. ASHCROFT N. W. and WILKENS J. W., *Phys. Lett.* **14**, 285 (1965).
15. KNIGHT W. D., *Solid State Physics* (Edited by F. Seitz and D. Turnbull), Vol. 2, Academic Press, New York (1956).
16. NARATH A. and WEAVER H. T., *Phys. Rev.* **175**, 373 (1968).
17. GASPARI G. D. and DAS T. P., *Phys. Rev.* **167**, 660 (1968).

VC, NbC AND TaC WITH VARYING CARBON CONTENT STUDIED BY ESCA*

LARS RAMQVIST

The Axel Johnson Institute for Industrial Research, Nynäshamn, Sweden

and

KJELL HAMRIN, GUNILLA JOHANSSON, ULRIK GELIUS and CARL NORDLING

Institute of Physics, Uppsala University, Uppsala, Sweden

(Received 18 February 1969; in revised form 24 October 1969)

Abstract—Electron spectroscopic studies by the ESCA technique of core level electrons in VC, NbC and TaC with varying carbon contents show that the electron transfer from the metal atoms increases with increasing carbon content in the VC phase but decreases in the NbC and TaC phases. The VC phase resembles the TiC phase measured in a previous investigation. The ESCA shifts are compared with heats of formation

1. INTRODUCTION

RECENT investigations [1, 2] on the variation of physical properties with carbon content of cubic carbides of Group 4b (TiC, ZrC, HfC), and Group 5b (VC, NbC, TaC) have shown that the NbC and TaC phases differ in many respects from the other phases. For example, the hardness was found to increase with increasing carbon content for Group 4b carbides and for the VC phase but to decrease in the NbC and TaC phases. These observations make it especially interesting to study the variation of the electronic structure with carbon content of Group 5b carbides and to correlate parameters pertaining to these variations to the variations of physical and chemical properties.

We have previously reported an investigation by the ESCA method [3] on transition metal carbides and related compounds [4]. We then studied *inter alia* the energy shifts of the core electrons in TiC with varying carbon content. The charge distribution in carbides was shown to be such that the

metal atoms are positive and the carbon atoms negative. It was also found that the $Ti2p_{3/2}$ binding energy increases with carbon content

TiC

between the electronic structure, physical and chemical properties of Group 4b and 5b is given in Ref. [5].

2. EXPERIMENTAL AND RESULTS

Properties of the hot-pressed test materials and reference metals are summarized in Table 1. The reference metals V, Nb and Ta were supplied by Johnson, Matthey & Co., Ltd. London, England. The preparation and analytic methods used are described in [4]. The electron spectroscopy technique used is described in [3] and [4].

When the electron spectra are induced by soft X-radiation, $AlK\alpha$ or $MgK\alpha$, one obtains narrow electron lines with high in-

*ESCA—Electron Spectroscopy for Chemical Analysis.

Table 1. Properties of the hot-pressed test materials and reference metals. Shifts in binding energy relative to pure elements. (Binding energies of pure elements are given in parentheses)

Carbide	C/Me + 0.003	a_0 Å	$\Sigma O, N, H$ (wt %)	Σ Me impurities (wt %)	$\Delta V2p_{3/2}$ ± 0.1 (eV)	$\Delta Nb3d_{5/2}$ ± 0.10 (eV)	$\Delta Ta4f_{7/2}$ ± 0.2 (eV)	ΔCls +0.2 (eV)
VC	0.876 0.716	4.1670 ± 0.0001 4.1250 ± 0.0003	0.09 0.11	< 0.1 < 0.1	1.8 1.5 ($V2p_{3/2} = 511.8$)			-2.6 -2.6
NbC	0.940 0.904 0.774	4.4676 ± 0.0001 4.4660 ± 0.0002 4.4495 ± 0.0002	0.06 0.07 0.09	< 0.5 < 0.5 < 0.5		1.24 1.28 1.40 ($Nb3d_{5/2} = 201.77$)		-2.9 -2.9 -3.0
TaC	0.990 0.963 0.887 0.743	4.4550 ± 0.0002 4.4514 ± 0.0001 4.4394 ± 0.0002 4.4200 ± 0.0001	0.07 0.07 0.09 0.12	< 0.1 < 0.1 < 0.1 < 0.1			1.6 1.7 1.6 1.8 ($Ta4f_{7/2} = 21.5$)	-2.9 -2.9 -2.9 -3.1 ($Cl_s = 285.0$)
Reference metal								
V				< 0.1				
Nb				< 0.3 (Ta)				
Ta				< 0.02				

tensities and well resolved from each other if suitable shells are studied. A high photoelectric cross-section is achieved if one chooses the shell with the lowest principal quantum number accessible. Of the different subshells within this shell one chooses to study the outermost one since the inner subshells are broadened due to Coster-Kronig transitions, sometimes to the extent that it is difficult to measure energy shifts for such levels.

In the present paper we present measurements of the $V2p_{3/2}$ level in V and VC_x ($x = 0.876$ and 0.716); of the $Nb3d_{5/2}$ level in Nb and NbC_x ($x = 0.940$, 0.904 and 0.744), and of the $Ta4f_{7/2}$ level in Ta and TaC_x ($x = 0.990$, 0.963 , 0.887 and 0.745). Excitation of the electron spectra was made by $AlK\alpha$ radiation.

In all carbides the electron binding energies of the metal component were shifted towards higher values relative to the pure metals indicating that electrons are transferred from the metal atom. It was found that the $V2p_{3/2}$

binding energy shift increases but that the $Nb3d_{5/2}$ and $Ta4f_{7/2}$ shifts decrease with increasing carbon content within the homogeneity ranges of the carbides. The results are given in Table 1 and Fig. 1. The $Ta4f_{7/2}$ level has probably too low a binding energy (23 eV) to be free from hybridization with the band. The interpretation of the $Ta4f_{7/2}$ shifts in terms of charge transfer is therefore somewhat uncertain.

The Cl_s level was also studied in the three carbide series. The carbon shifts are negative referred to carbon in the hydrocarbon layer which is used for calibration of the spectra. This is a further indication that electrons are transferred to the carbon atoms. It is interesting to notice that the carbon binding energy is almost a constant for each carbide phase, indicating that each carbon atom receives the same amount of electrons when introduced in the lattice.

The metal lines from the non-stoichiometric carbides were broader than the corresponding lines from the stoichiometric carbide and

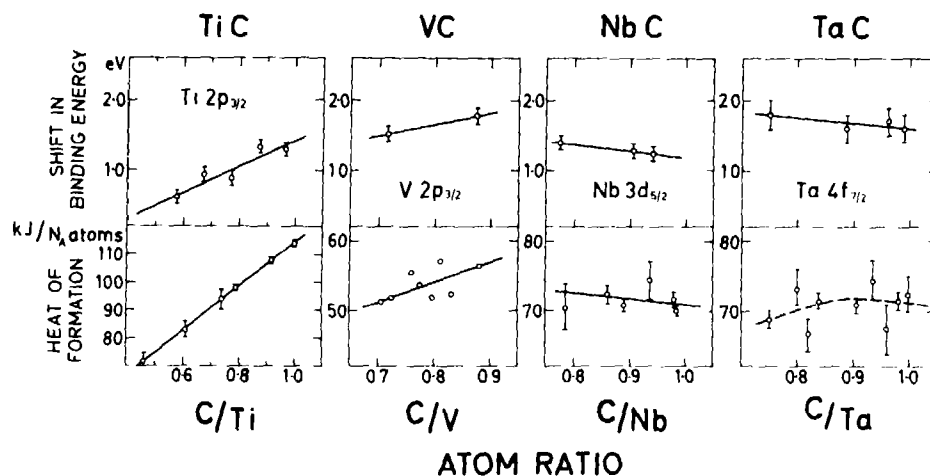


Fig. 1 Binding energy shifts of core electrons and heats of formation vs. atom ratio x for TiC_x , VC_x , NbC_x and TaC_x within the homogeneity ranges of the carbides. The heats of formation were obtained from Refs. [6–9, 11].

the pure metal. This broadening is due to the fact that not all metal atoms have the same number of metal–carbon bonds. A similar broadening is not expected for carbon since carbon has always six metal atoms as nearest neighbours.

3. DISCUSSION

Although only small differences in binding energy were measured by ESCA between carbides with different carbon content it can be claimed that the NbC and TaC phases differ from the VC phase and the previously measured TiC phase. Judging from the ESCA shifts the electron transfer from the metal atoms increases with increasing carbon content in the TiC and VC phases but decreases in the NbC and TaC phases.

The variations of the heat of formation with carbon content of VC, NbC and TaC have been reported in the literature [6–9]. The function for TaC resembles that of NbC [5, 9]. As discussed in [4] and [5] bond strength in MeC_x can be represented by $(-\Delta H_{298\text{K}}/1+x)\text{kJ per } N_A \text{ atoms}$, where $-\Delta H_{298\text{K}}$ is

the heat of formation per mole and N_A is Avogadro's number.

Figure 1 shows that the heats of formation per

since

shifts are proportional to the quantity $-\Delta H_{298\text{K}}/1+x$, which is a measure of the variation of the bond strength, ESCA shifts may be used as a measure of the variations of the bond strength in cubic carbides within the homogeneity range. Furthermore, since ESCA measures charge transfer, Fig. 1 suggests that the variation of heat of formation with composition is mainly due to a change in the ionic contribution to the bond. The covalent contribution to the bond may also change with composition. Except for the VC phase this is in agreement with the localized molecular orbital model for cubic refractory compounds given by Denker [10]. Although

he does not discuss Group 4b contra 5b carbides at any length it is evident from Denker's model that the bond strength in Group 5b carbides should decrease with increasing carbon content due to filling of the anti-bonding orbitals which are predominantly localized around the metal atoms. Since the metal atoms in the carbides have positive charge this also implies decreasing ionic contribution to the bond when adding carbon atoms.

For a comparison the TiC phase[4] is also shown in Fig. 1. It is noteworthy that the changes of both the core electron energy as measured by ESCA and the heat of formation [11] are larger for this phase than for the VC, NbC and TaC phases. The variation of electron transfer measured by electron spectroscopy and the variation of bond strength with composition of carbides of Group 4b and 5b illustrated in Fig. 1, also give a qualitative explanation of the variations of recently measured properties like lattice parameter, hardness, resistivity and wetting by liquid metals [5].

Acknowledgement—We thank Professor Kai Siegbahn for his interest in this investigation.

REFERENCES

1. RAMQVIST L., *Jernkont. Ann.* **152**, 465 (1968)
2. RAMQVIST L., *ibid.* **152**, 517 (1968)
3. SIEGBAHN K., NORDLING C., FAHLMAN A., NORDBERG R., HAMRIN K., HEDMAN J., JOHANSSON G., BERGMARK T., KARLSSON S.-E., LINDGREN I. and LINDBERG B., ESCA, Atomic, molecular and solid state structure studied by means of electron spectroscopy *Nova Acta Regiae Soc. Sci. Upsal. Ser. IV*, Vol. 20 (1967).
4. RAMQVIST L., HAMRIN K., JOHANSSON G., FAHLMAN A. and NORDLING C., *J. Phys. Chem. Solids* **30**, 1835 (1969)
5. RAMQVIST L., *Jernkont. Ann.* **153**, 159 (1969)
6. VOLKOVA N. M. and GEI'D P. V., *Izv. Vysstrikh Uchebn. Zavedeni. Tsvetn. Met.* **3**, 77 (1965).
7. HUBER Jr. E. Y., HEAD E. L., HOLLEY Jr. C. E., STORMS F. K. and KRIKORIAN N. H., *J. phys. Chem.* **65**, 1846 (1961).
8. HUBER Jr. E. Y., HEAD E. L., HOLLEY Jr. C. E. and BOWMAN A. L., *J. Phys. Chem.* **67**, 793 (1963).
9. STORMS F. K. *The Refractory Carbides*, Academic Press, New York (1967)
10. DENKER S. P. *J. less-common Metals* **14**, 1 (1968).
11. MOROZOVA M. P., KHRIPUN M. K. and ARIYA S. M., *Zh. Obshchei Khim.* **32**, 2072 (1962) (English translation)

LOW-TEMPERATURE HEAT CAPACITIES OF THE CLATHRATE SALTS $\text{Ag}_7\text{O}_8\text{NO}_3$ AND $\text{Ag}_7\text{O}_8\text{HF}_2$ *

MARY M. CONWAY† and NORMAN E. PHILLIPS

Inorganic Materials Research Division of the Lawrence Radiation Laboratory and Department of Chemistry, University of California, Berkeley, Calif. 94721, U.S.A.

and

T. H. GEBELLE‡ and N. A. KUEBLER

Bell Telephone Laboratories, Murray Hill, N.J. 07971, U.S.A.

(Received 12 January 1969)

Abstract—The heat capacities of $\text{Ag}_7\text{O}_8\text{NO}_3$ and $\text{Ag}_7\text{O}_8\text{HF}_2$ have been measured between 0.3 and, respectively, 20 and 4°K. The measurements show that the previously reported type II superconductivity is a bulk property, and give the values of some of the normal and superconducting-state parameters. There is a surprisingly strong dependence of the electronic density of states and Debye temperature on anion identity, but no convincing evidence for a direct effect of anion identity on T_c .

1. INTRODUCTION

THE SILVER-oxide clathrate salts Ag_7O_8X^- with $X^- = \text{NO}_3^-$, HF_2^- , BF_4^- , F^- are the only known examples of clathrates that exhibit metallic conductivity. For the NO_3^- salt, residual resistance ratios, $\zeta(300^\circ\text{K})/\zeta(4.2^\circ\text{K})$, as high as 200 have been observed, and the phonon resistivity varies as $T^{3.5}$ below 12 K [1]. These salts also undergo superconducting transitions. The transition temperatures T_c , as determined by magnetic measurements, were originally reported as 0.15, 0.3 and 1.04°K for the BF_4^- , F^- and NO_3^- salts respectively [1]. Later measurements showed that the samples of the F^- salt had contained paramagnetic impurities and that samples of the HF_2^- salt have transition temperatures of 1–1.5°K [2].

The crystal structure is based on face-sharing, 26-sided, Ag_6O_8 polyhedra. Oxygen atoms are located at the 24 corners (each common to 3 polyhedra) and Ag atoms at the

centers of the 12 square faces (out of 18) that are common to 2 polyhedra. Cubic spaces between the polyhedra, equal in number to the polyhedra, contain the one additional Ag atom per unit cell.

... has not been established. It seems probable that both transitions are associated with the anions taking up regular orientations in the cage. The salts with the more symmetrical F^- and BF_4^- anions apparently remain cubic at low temperature [1]. The room-temperature cubic unit cell dimensions of the HF_2^- , F^- , NO_3^- and BF_4^- salts are 9.824, 9.833, 9.893 and 9.942 Å, respectively [1, 2].

The heat capacity measurements on $\text{Ag}_7\text{O}_8\text{NO}_3$ and $\text{Ag}_7\text{O}_8\text{HF}_2$ reported here were undertaken to verify the existence of bulk superconductivity and to obtain values of the related normal-state parameters $N(0)$, the density of electronic states at the Fermi

*Work at Berkeley supported by the U.S. Atomic Energy Commission; work at Stanford supported by A.F.O.S.R. Grant 68-1510B.

†National Science Foundation Graduate Fellow.

‡Also at Stanford University, Stanford, Calif. 94305, U.S.A.

energy, and θ_0 , the Debye characteristic temperature at 0°K. It was hoped that a comparison of these parameters and T_c for different salts might provide a basis for deciding whether or not vibrational modes associated with the loosely bound anions played a role in determining the superconducting state properties. The possible importance of anion vibrational modes is of course suggested by the strong variation in T_c produced by changing the anion. The NO_3^- salt was chosen for study because it showed the sharpest transition. The other three salts known to become superconducting all show broader transitions (apparently because of the presence of small amounts of a paramagnetic impurity, possibly silver ion in the d^9 configuration) and the HF_2^- salt was chosen primarily for its high transition temperature.

2. RESULTS

The heat capacity measurements were made on samples consisting of small crystals with dimensions on the order of a few millimeters. Thermal contact with a copper calorimeter was made with a small amount of

silicone oil. The heat capacities of the calorimeter and oil were measured separately. Temperature was measured with a germanium thermometer that had been calibrated against a cerium magnesium nitrate thermometer (0.25–1°K), the 1958 He^4 vapor-pressure scale (1–4°K), and a gas thermometer (4–20°K). The results below 2°K, in several magnetic fields, are shown in Fig. 1 as C/T vs. T^2 .

The heat capacity of $\text{Ag}_7\text{O}_8\text{NO}_3$ in the normal state shows the temperature dependence expected for a metal at very low temperatures.

$$C = \gamma T + (12/5)\pi^4 R (T/\theta_0)^3, \quad (1)$$

where γ is a constant proportional to $N(O)$. In 2400 Oe, the heat capacity of $\text{Ag}_7\text{O}_8\text{HF}_2$ includes a term proportional to T^{-2} which is believed to be a consequence of the presence of paramagnetic impurities: it would require 0.04 moles of free-electron spins per mole of $\text{Ag}_7\text{O}_8\text{HF}_2$ to produce an effect of this magnitude. The coefficient of this term was determined from the 0–°K intercept of a plot

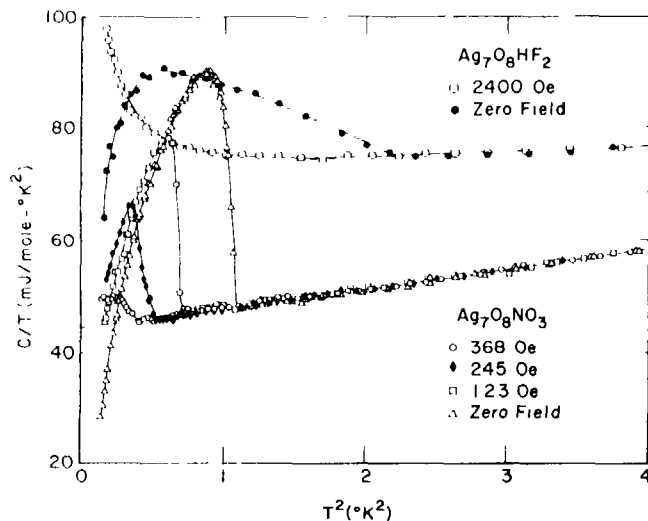


Fig. 1 The heat capacities of $\text{Ag}_7\text{O}_8\text{HF}_2$ and $\text{Ag}_7\text{O}_8\text{NO}_3$. Only the data for $T < 2^\circ\text{K}$ are shown

of CT^2 vs. T^3 and the T^{-2} term was subtracted from the total heat capacity to obtain the dashed line shown in Fig. 1 for $\text{Ag}_7\text{O}_8\text{HF}_2$ in the normal state. The γ and θ_D values corresponding to the dashed lines in Fig. 1 are given in Table 1. All values are calculated for the molar formula $\text{Ag}_7\text{O}_8\text{X}$, which corresponds to one primitive unit cell. The variation of θ with T is shown for both salts in Fig. 2.

In zero magnetic field, the heat capacity of the $\text{Ag}_7\text{O}_8\text{NO}_3$ exhibits the temperature dependence expected for a slightly broadened superconducting transition: on cooling, the transition begins at 1.046°K and is 90 per cent complete (as estimated from the magnitude of the heat capacity) at 1.004°K . The lowest temperature zero-field data were corrected for the lattice heat capacity and fitted to the BCS expression[5] for the superconducting-state electronic heat capacity,

$$C_{es} = a \gamma T_c \exp(-bT_c/T). \quad (2)$$

With T_c taken as 1.025°K (see below) this

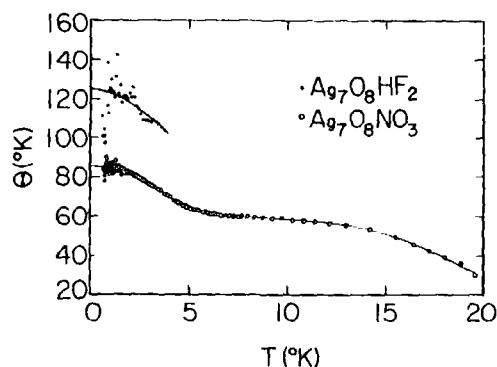


Fig. 2. The Debye characteristic temperatures of $\text{Ag}_7\text{O}_8\text{HF}_2$ and $\text{Ag}_7\text{O}_8\text{NO}_3$.

expression fits the data for $T_c/T > 1.7$ with $a = 6.12$ and $b = 1.22$, as shown in Fig. 3. The superconducting-state entropy, obtained by integration of the heat capacity (using extrapolated values below 0.38°K and above 0.94°K) is equal to the normal-state entropy at 1.025°K , and this temperature, which also corresponds approximately to the middle of the drop in heat capacity, has been taken as T_c . The critical magnetic field, calculated by a second integration, has a 0°K value $H_c(0) = 130$ Oe, and a maximum deviation from parabolic temperature dependence of -6 per cent.

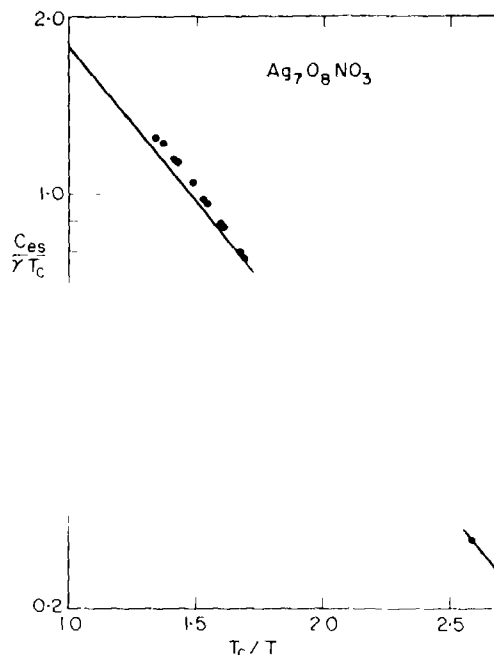


Fig. 3. The superconducting-state electronic heat capacity of $\text{Ag}_7\text{O}_8\text{NO}_3$.

Table 1. Normal-and superconducting-state parameters of $\text{Ag}_7\text{O}_8\text{HF}_2$ and $\text{Ag}_7\text{O}_8\text{NO}_3$

	γ ($\text{mJ}/\text{mole} \cdot ^\circ\text{K}^2$)	θ_D ($^\circ\text{K}$)	T_c ($^\circ\text{K}$)	$H_c(0)$ (Oe)
$\text{Ag}_7\text{O}_8\text{HF}_2$	72.5	125	0.8-1.5	
$\text{Ag}_7\text{O}_8\text{NO}_3$	44.6	85.3	1.025	130

The superconducting transition of $\text{Ag}_7\text{O}_8\text{NO}_4$ is shifted to lower temperatures with increasing magnetic field in the way expected for type-II superconductivity. The in-field transition occurs at the temperature at which the upper critical field $H_{c2}(T)$ is equal to the applied field. This temperature was taken as that of the midpoint of the drop in heat capacity. The three values of $H_{c2}(T)$ determined from the three heat capacities taken in magnetic fields were used to calculate the Landau-Ginsburg parameter, defined by [6] $\kappa = H_{c2}(T)/\sqrt{2}H_c(T)$. κ was found to be 2.2, 2.6 and 3.2 at 0.82, 0.67 and 0.58°K, respectively. These values do not fit the temperature dependence of κ predicted by the usual theories, but the discrepancy cannot be regarded as significant in view of the breadth of the transitions observed in higher magnetic fields and the resulting uncertainty in $H_{c2}(T)$.

The zero-field superconducting transition of $\text{Ag}_7\text{O}_8\text{HF}_2$ is broadened considerably, presumably by the paramagnetic impurities responsible for the T^{-2} term in the normal-state heat capacity. It seems reasonable to suppose that the transition has also been lowered by the same mechanism and that T_c for the pure salt may be considerably higher than 1.5°K. The breadth of the transition prevented an evaluation of the other superconducting-state parameters and, for the same reason, no attempt was made to study the depression of the transition in small magnetic fields.

The transition temperatures obtained for both salts are in good agreement with the values obtained from magnetic measurements, but the values of $H_c(0)$, γ , and κ obtained for the NO_3 -salt do not agree with the values obtained from magnetic measurements. Robin *et al.* calculated $H_c(0) = 57$ Oe from the area under a magnetization curve at 0.1°K and, with the assumption of a parabolic dependence of H_c on T , found $\gamma = 7.3$ mJ/mole-°K². They also estimated $\kappa \approx 100$ from the shape of the magnetization curve. It seems clear that the values of γ and $H_c(0)$

must be given correctly by the calorimetric measurements. (Measurements on a second sample, not reported here, gave essentially identical results.) On the other hand, it is not at all clear why the magnetic measurements gave such different values. Possibly the discrepancy is related to the different physical condition of the samples: the magnetic measurements were made on powdered material and the calorimetric samples consisted of small crystals.

3. DISCUSSION

Substitution of an HF_2^- ion for an NO_3^- ion produces a volume contraction of only 2.1 per cent, but increases θ_0 from 85.3 to 125°K. This effect, which would correspond to a Gruneisen constant of ≈ 18 , is an order of magnitude larger than would be expected for a pressure-induced contraction in an ordinary lattice.

With increasing temperature, there are two distinct drops in the value of θ for the NO_3 salt. The initial drop, from 82.5°K near 0°K to ≈ 60 °K in the 5–10°K region is typical of that observed in many solids and is of a magnitude often associated with phonon dispersion. However, the second drop, which occurs above 15°K, is unusual. It is very probably associated with a rocking mode of the NO_3 ion, but the lack of measurements on the HF_2 salt in this temperature region make this interpretation somewhat speculative.

The HF_2 salt shows only a temperature-independent paramagnetic susceptibility, and Hall-effect measurements indicate the presence of between two and three carriers per Ag_6O_8 unit. It has been suggested that the A_g atoms in the Ag_6O_8 units are in the diamagnet $4d^8$ square-planer configuration, and that the two remaining electrons are in a conduction band that utilizes the $4d$ orbitals of the Ag atoms and the $2p$ orbitals of the O atoms [2]. The free-electron γ value corresponding to this electron density (which is not very sensitive to the exact number of electrons) is 4.8 mJ/mole-°K. The observed γ

values are considerably higher—44.6 and 72.5 mJ/mole-°K² for the NO₃⁻ and HF₂⁻ salts, respectively—showing that $N(O)$ is much greater than for free electrons, and suggesting that the conduction band is very narrow. Since there is very little conduction electron density at the anion[2], the difference in $N(O)$ between the two salts must be attributed mainly to the different Ag-O distances. The effect of lattice parameter on $N(O)$ is also surprisingly large—a 2.1 per cent reduction in volume is accompanied by a 62 per cent increase in $N(O)$.

The possibility that the anions contribute directly to the superconducting interaction in these salts can be tested by comparing the observed critical temperatures with theoretical expressions that relate T_c to normal-state properties. (The theoretical expressions also contain quantities that are not known independently, and it is necessary to rely on empirical correlations between these quantities and other properties.) The value of T_c is known accurately only for the NO₃⁻ salt, and we shall start from that value and estimate T_c for the pure HF₂⁻ salt on the assumption that in both cases the only important interactions between electrons are the coulomb repulsion and the attractive interaction via acoustic phonons. First, however, it is useful to consider the probable effect of the magnetic impurities on the critical temperature of the HF₂⁻ salt. On the assumption that the observed broadening of the transition is produced by magnetic impurities, the value of T_c for the pure HF₂⁻ salt must be at least 1.5°K, the highest temperature at which the zero-field heat capacity deviates from the normal-state value. A theoretical treatment[7], which has been partially confirmed by experimental data [8, 9], predicts an approximately linear decrease in the energy gap and in T_c with increasing concentration of paramagnetic impurities, for concentrations that are not too high. The fractional decrease in the energy gap is approximately double the fractional decrease in T_c for the same impurity con-

centration. The theory is not sufficiently complete to allow a detailed comparison with the superconducting-state heat capacity of the HF₂⁻ salt. However, the lowest-temperature zero-field heat capacity data for the HF₂⁻ salt show a sharp drop with decreasing temperature suggesting the presence of a significant energy gap and T_c for the pure material is therefore unlikely to be higher than about 5°K.

The BCS theory[5] represents the phonon spectrum and the electron-electron interactions by single parameters— θ_0 and V , respectively—and gives the critical temperature as

$$T_c = 0.855 \theta_0 \exp \{-1/N(O)V\}. \quad (3)$$

The values of V deduced by application of this equation to experimental values of T_c , θ_0 , and $N(O)$ vary considerably from one superconductor to another. However, if the numerical coefficient 0.855 is replaced by an adjustable parameter, the experimental data for

relate

For a typical solid the average frequency would be lower relative to θ_0 and the correct value of the numerical coefficient would therefore be somewhat less than 0.855.) If it is assumed that V has the same value for the NO₃⁻ and HF₂⁻ salts, T_c for the HF₂⁻ salt can be predicted from that of the NO₃⁻ salt and the various normal-state parameters. Using equation (3), the predicted T_c for the HF₂⁻ salt is 7.8°K, and, if the numerical coefficient is changed to 0.4, the predicted T_c becomes 5.8°K. Thus, the T_c of pure Ag₇O₈HF₂ does not appear to differ significantly from the value expected from the T_c of Ag₇O₈NO₃ and the normal-state parameters.

McMillan[11] has given a more exact treatment of the electron-electron interactions, and derived, for the critical temperature,

$$T_c = 0.69 \theta_D \exp \left[-\frac{1.04(1+\lambda)}{\lambda - u^* (1 + 0.62\lambda)} \right]. \quad (4)$$

In the derivation, a particular phonon spectrum (that of niobium) was assumed but the result is expected to be valid for all weak-coupling ($\lambda < 1$) superconductors. The coulomb repulsion u^* is approximately 0.10 for simple metals and 0.13 for transition metals. The attractive phonon interaction λ is proportional to the 'bare' or band-structure density of states, $N_{bs}(O) = N(O)/(1+\lambda)$, and for certain alloy systems $N_{bs}(O)$ seems to dominate the dependence of λ on concentration[12]. (The dominance of the $N_{bs}(O)$ factor is closely related to the validity of equation (3) with a constant V and modified numerical factor.) A comparison of the critical temperatures of $\text{Ag}_7\text{O}_8\text{NO}_3$ and $\text{Ag}_7\text{O}_8\text{HF}_2$ on the basis of equation (4) and the assumption that λ is dominated by $N_{bs}(O)$ is very similar to that based on equation (3). With $u^* \approx 0.13$, and T_c for the HF_2^- salt taken as the highest observed value, 1.5°K, λ has the same value for both salts—0.57. If λ were proportional to $N_{bs}(O)$ the values of λ and T_c for the HF_2^- salt would be larger relative to those for the NO_3^- salt—0.81 and 4°K, respectively—but the discrepancy is not large enough to be significant.

Although some data indicates that λ is proportional to $N_{bs}(O)$, McMillan has suggested, on the basis of other empirical evidence, that the dependence on $N_{bs}(O)$ is cancelled by other factors in λ and that within a given class of superconductors λ is inversely proportional to the square of a certain average of the phonon frequencies[11]. On this basis the values of λ and T_c for the HF_2^- salt would be predicted to be much lower relative to the values for the NO_3^- salt—0.27 and 10°K, respectively. This would suggest that the superconducting interaction in the HF_2^- salt

is in some way enhanced over that in the NO_3^- salt. However, the correlation on which this comparison is based is not well established—the number of examples that have been found to support it is small, and its role in those cases in which λ is proportional to $N_{bs}(O)$ is not clear.

4. CONCLUSION

The previously reported superconductivity of $\text{Ag}_7\text{O}_8\text{NO}_3$ and $\text{Ag}_7\text{O}_8\text{HF}_2$ is a bulk property. All samples of the HF_2^- salt that have been investigated so far have probably contained enough magnetic impurities to depress the critical temperature, and the critical temperature of pure material is probably higher than 1.5°K, but less than 5°K.

The electronic density of states and the phonon frequencies of the silver oxide cage structure are extremely sensitive to the changes in lattice parameter associated with changes in anion size. Apart from this indirect effect, there is as yet no clear indication that the anion plays any role in the superconductivity of these salts.

REFERENCES

1. ROBIN M. B., ANDRES K., GEBALLE T. H., KUEBLER N. A. and McWHAN D. B., *Phys. Rev. Lett.* **17**, 917 (1966).
2. GOSSARD A. C., HINDERMAN D. K., ROBIN M. B., KUEBLER N. A., and GEBALLE T. H., *J. Am. chem. Soc.* **89**, 7121 (1967).
3. KUNG-DU C., *Scientia sin.* **12**, 139 (1963).
4. NÁRAY-SZABO I., ARGAY G. and SZABO P., *Acta. crystallogr.* **19**, 180 (1965).
5. BARDEEN J., COOPER L., and SCHIEFFER J. R., *Phys. Rev.* **108**, 1175 (1957).
6. ABRIKOSOV A. A., *Zh. eksp. teor. Fiz.* **32**, 1442 (1957); English transl: *Soviet Phys. JETP* **5**, 1174 (1957); *J. Phys. Chem. Solids* **2**, 199 (1957).
7. SKALSKI S., BEIHEDER-MATIBET O., and WEISS P. R., *Phys. Rev.* **136**, A1500 (1964).
8. WOLF M. A. and REIF E., *Phys. Rev.* **137**, A557 (1965).
9. FINNEMORE D. K., JOHNSON D. I., OSTENSON J. E., SPEDDING F. H. and BEAUDRY B. J., *Phys. Rev.* **137**, A550 (1965).
10. See, for example, BUCHER E., HEINIGER F., MUHEIM J. and MÜLLER J., *Rev. mod. Phys.* **36**, 146 (1964).
11. McMILLAN W. L., *Phys. Rev.* **167**, 331 (1968).
12. See Fig. 9 of Ref. [11].

SURFACE STATE PARAMETERS OF METAL-FREE PHTHALOCYANINE SINGLE CRYSTALS

D. F. BARBE

Westinghouse Aerospace Division, Baltimore, Md. 21203, U.S.A.

and

C. R. WESTGATE

The Johns Hopkins University, Baltimore, Md. 21218, U.S.A.

(Received 29 December 1969; in revised form 24 March 1970)

Abstract—Field-effect measurements have been performed on single crystals of metal-free phthalocyanine in high vacuum, hydrogen, and oxygen ambients. The effect of localized bulk states was taken into account. The usual field-effect analysis was modified to take into account the variation of the channel-to-gate potential along the channel. D.C. measurements indicate the presence of at least 10^{11} cm^{-2} slow surface states. The time constant of these states is dependent on the ambient gas. Transient field-effect measurements indicate the presence of three sets of fast surface states having densities of 10^{10} – 10^{11} cm^{-2} within 0.17 eV of midgap. The parameters of these surface states are not appreciably affected by ambient gases. The thickness of the space-charge region of metal-free phthalocyanine crystals is 10^{-5} – 10^{-4} cm .

1. INTRODUCTION

THE EXISTENCE of electronic states whose wavefunctions are located at the surface of a solid; i.e. surface states, is well known[1]. The equilibrium charge in surface states is determined by (1) the density of surface states, (2) their proximity to the Fermi level, and (3) their type; i.e. donor type or acceptor type. Surface states are further characterized by the degree of communication with the bulk. States which are in intimate contact with the bulk are called 'fast' surface states, and those in poor contact with the bulk are called 'slow' surface states. Fast surface states are usually attributed to the effect of the termination of the crystal lattice at the surface, and slow states are usually due to foreign atoms adsorbed on the surface. The time constants associated with fast and slow surface states are usually orders of magnitude apart. This allows the fast and slow surface states to be studied separately using a.c. or transient techniques.

The effect of charge in surface states (Q_{ss}) is to set up an electric field ($E = Q_{ss}/2\epsilon$) which extends into the solid. As a result, the energy

bands bend in such a way that the concomitant space charge exactly cancels the charge in

by Q_{ss} surface, i.e. the net charge is zero. Surface-state parameters; i.e. type, energy, and density, can be determined by comparing the measured surface conductance with the calculated conductance of the space charge region[2].

The history of surface studies on molecular solids is relatively short. D.C. field-effect measurements were performed by Heilmeyer and Zanoni[3] on α -form copper phthalocyanine films. Their order-of-magnitude analysis indicated the presence of about 10^{13} cm^{-2} surface states. Baessler and Vaubel [4] studied the photoemission of electrons and holes from various metals into anthracene crystals and concluded that the density of

surface states on anthracene crystals was about $2.10^{13} \text{ cm}^{-2} \text{ eV}^{-1}$. Usov and Benderskii [5] studied the photoconductivity of metal-free and magnesium phthalocyanine films by a pulse method. They reported surface barrier heights of 0.1–0.5 eV, barrier thicknesses of about 10^{-5} cm , and densities of trapped carriers of 10^{15} – 10^{16} cm^{-3} .

The purpose of the work described in this paper is to make an accurate determination of the surface-state parameters for single crystals of metal-free phthalocyanine in order to resolve the influence of surface states on conduction properties. We have reported in previous papers that metal-free phthalocyanine crystals have large densities of localized bulk states [6–8]. In order to interpret field effect data on these crystals, two factors must be taken into account: (1) the effect of the localized bulk states on the characteristics of the space charge region and (2) the variation of the gate-to-surface potential along the surface from source to drain.

The outline of this paper is as follows: We first give the equations which govern the behavior of the space charge region when localized states are taken into account. The variation of the gate-to-surface potential is taken into account by defining an effective gate voltage. The field-effect data are then analyzed in the usual way. The surface-state parameters are determined by fitting the field-effect data with terms representing surface states at discrete energies.

2. THEORY

For a semiconductor having localized electron and hole states at discrete energies, the first integration of Poisson's equation can be performed analytically and is given by the following set of equations [9]. An energy diagram illustrating the definitions is given in Fig. 1.

$$\frac{dy}{dx} = F(y) = \pm \sqrt{\frac{2e^2}{\epsilon kT}} [f_1(n_i, u_b, y) + f_2(N_m, \varphi_m, y) + f_3(P_n, \theta_n, y)]^{1/2}, \quad (1)$$

where ϵ = dielectric constant of the crystal ($\epsilon = \kappa \epsilon_0$),

e = magnitude of electronic charge,

k = Boltzmann's constant, and

T = absolute temperature of the crystal.

$$f_1 = 2n_i [\cosh(u_b + y) - \cosh(u_b) - y \sinh(u_b)], \quad (2)$$

n_i = intrinsic density of carriers,

$$u(x) = [E_F - E_i(x)]/kT, \quad (3)$$

$$u_b = [E_F - E_{ib}]/kT, \quad (4)$$

E_F = Fermi energy of the crystal,

$E_i(x)$ = the energy level which has the same curvature as the band edges and in the bulk coincides with the intrinsic Fermi level, E_{ib} , and

$y(x) = u(x) - u_b$ = amount of band bending in units of kT . (5)

$$f_2 = \sum_m N_m \left[\ln \left\{ 1 + \frac{\exp(y) - 1}{1 + \exp(\varphi_m)} \right\} - \frac{y}{1 + \exp(\varphi_m)} \right], \quad (6)$$

where N_m is the density of localized electron states (LES) at an energy E_m , and

$$\varphi_m = [E_m - E_F]/kT + \ln\left(\frac{1}{2}\right). \quad (7)$$

The term $\ln\left(\frac{1}{2}\right)$ in equation (7) occurs because we assume that each state can be occupied by one electron regardless of spin.

$$f_3 = - \sum_n P_n \left[\ln \left\{ 1 + \frac{\exp(-y) - 1}{1 + \exp(-\theta_n)} \right\} + \frac{y}{1 + \exp(-\theta_n)} \right], \quad (8)$$

where P_n is the density of localized hole states (LHS) at an energy E_n , and

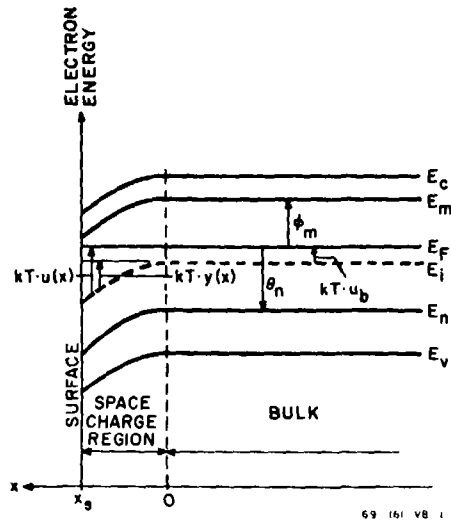


Fig. 1. Energy band diagram showing the definitions of u_b , $u(x)$, $y(x)$, ϕ_m and θ_n .

$$\theta_n = [E_n - E_F]/kT - \ln(2). \quad (9)$$

The function f_1 accounts for the contribution to the space-charge density of electrons in the conduction band and holes in the valence band. The functions f_2 and f_3 account for space charge due to electrons in IES and holes in LHS respectively. We assume that the IES are acceptor-type states and that the LHS are donor-type states.

The characteristics of the space-charge region can be calculated as follows: The space charge per unit area is given by equation (10).

$$Q_{sc} = (-ekT/e)F(y_s), \quad (10)$$

where y_s is the value of y at the surface. The change in the surface conductance is given by equation (11).

$$\begin{aligned} \Delta G_{\text{calc.}} &= (G - G_{\text{min}})_{\text{calc.}} \\ &= \frac{n_i e}{2} \left[\mu_r \int_0^{y_s} \frac{\exp(y + u_b) - \exp(u_b)}{F(y)} dy \right. \\ &\quad \left. + \mu_h \int_0^{y_s} \frac{\exp(-y - u_b) - \exp(-u_b)}{F(y)} dy \right], \quad (11) \end{aligned}$$

where μ_r is the mobility of electrons in the conduction band and μ_h is the mobility of holes in the valence band. The shape of the band bending at the surface can also be determined from equation (1) by inverting and integrating; i.e.

$$x(y) - x(y_r) = \int_{y_r}^y dy' / F(y'), \quad (12)$$

where y_r is an arbitrary value of y which is chosen as a reference.

The curve of $(\Delta G)_{\text{calc.}}$ vs. Q_{sc} can be calculated from equations (10) and (11) by using y_s as the parameter. This curve gives the change in surface conductance, ΔG , due to an induced surface charge density $Q_{\text{ind}} = Q_{sc}$ when there are no surface states; i.e. when all of the induced charge resides in the space-charge region. Because of the effect of localized bulk states (IES and LHS) on the form of equations (10) and (11), the operation indicated in equation (11) cannot be performed.

from (1)

voltage, V_g , is much larger than the drain voltage, V_d ; i.e. when $|V_g| \gg |V_d|$, the variation of the surface-to-gate potential, $V(z)$, is negligible; i.e. $V(z) = V_g$ (z is the distance from the source toward the drain along the surface). In this case, the induced charge per unit area is given by equation (13)

$$|Q_{\text{ind}}| = C_a |V_g|, \quad (13)$$

and the source-to-drain resistance is given by equation (14)

$$R_{sd} = \frac{l/w}{\mu \theta C_a |V_g|}, \quad (14)$$

where C_a = geometrical capacitance per unit area between the gate electrode and the semiconductor surface,

l = channel length,

w = channel width,

μ = mobility of the majority carriers in the channel, and

θ = fraction of induced charge which is mobile.

For high resistivity crystals, it is not always possible to make a complete set of field-effect measurements with $|V_g| \gg |V_d|$; in fact, to obtain measurable currents it may be necessary to have $|V_d| > |V_g|$. With V_g and V_d of the same polarity, it is possible to have a p - n junction induced into the channel, in which case no clear interpretation of field-effect data is possible. On the other hand, if V_g and V_d are of opposite polarity only charge of one type is induced; in this case, field-effect data can be interpreted if the effect of the variation of $V(z)$ on the source-to-drain resistance is taken into account. We accomplish this by introducing an effective gate voltage, V_{eff} , defined by equation (15):

$$R_{sd} = \int_0^l \frac{dz/w}{\mu \theta C_a V(z)} = \frac{l/w}{\mu \theta C_a V_{eff}}. \quad (15)$$

For V_g and V_d of opposite polarity and for transverse fields in the range where the channel mobility is field independent, V_{eff} is given by equation (16) [10].

$$V_{eff} = |V_g| + \frac{1}{2}|V_d|, \quad (16)$$

and the effective induced charge is given by equation (17)

$$Q_{ind} = C_a (|V_g| + \frac{1}{2}|V_d|). \quad (17)$$

The change in surface conductance, $(\Delta G)_{exp}$, can be calculated from drain current measurements via equation (18)

$$(\Delta G)_{exp} = \{(l/w)(I - I_{min})\}/V_d, \quad (18)$$

where I is the drain current, and I_{min} is the minimum drain current.

3. EXPERIMENTAL DETAILS

The field-effect configuration used for the measurements is shown in Fig. 2. Quartz was used as the substrate because of its very high surface resistivity. Mylar pads were used to give a one mil spacing between the gate electrode and the semiconductor surface. A grounded guard ring was used to shunt current leaking across the substrate from the gate or drain to ground thereby preventing it from flowing through the electrometer.

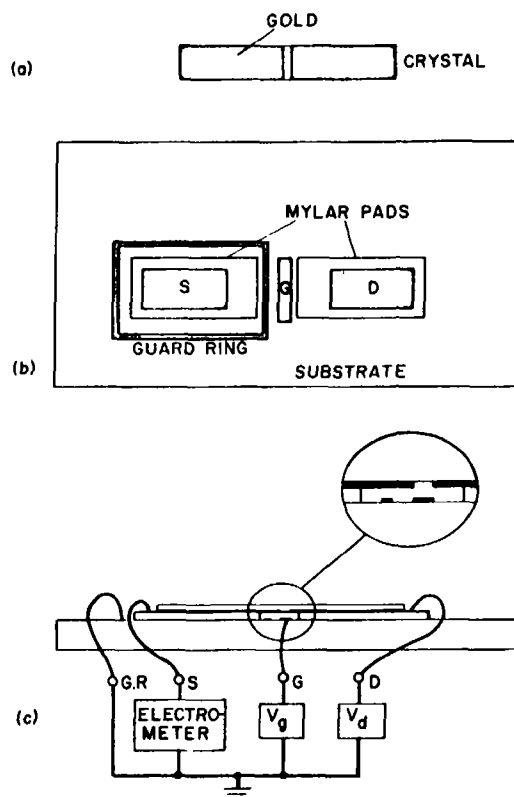


Fig. 2. The field-effect configuration. (a) The metallization pattern on the crystal, (b) The metallization pattern and mylar pads on the substrate, (c) The electrical connections used. The insert shows the detailed nature of the gate and channel regions.

Wide crystals having flat surfaces were chosen for the experiments. The crystals were grown by sublimating crude metal-free phthalocyanine (Eastman) in a two-zone global furnace using nitrogen gas as the carrier. This method is described in detail elsewhere [7, 11]. The crystals used in the field-effect experiments were from the same growths as those for which bulk measurements were reported earlier [7, 8]. The crystals were stored in a dessicator, and no chemical treatment was used.

The field-effect structure shown in Fig. 2 was mounted in a vacsorb-vacion system, and the system was pumped down to $5 \cdot 10^{-9}$ torr. Pumping was continued until the source-to-drain resistance stabilized. This usually required 24–36 hr. After field-effect measurements were made in vacuum, hydrogen was let into the system until a pressure of 1 atm was attained. Field-effect measurements were made after the source-to-drain resistance had stabilized. The system was again pumped down until the original results in vacuum were repeated. The cycle was then repeated using oxygen instead of hydrogen.

4. EXPERIMENTAL RESULTS

D.C. field-effect experiments were made of five crystals for gate voltages up to 500 V and for drain voltages up to 200 V. In each case, no d.c. field effect was observed. For $V_g = 500$ V, approximately 10^{11} carriers per cm^2 are induced into the crystal; therefore, the total density of surface states, fast and slow, must be at least 10^{11} cm^{-2} .

Although no d.c. field effect was observed, transient field-effect measurements did yield meaningful results. When a step voltage is applied to the gate, displacement current flows until the gate-to-surface capacitance is charged. Since V_g and V_d are of opposite polarity, the direction of the charging current through the electrometer is opposite to the increase in current due to enhanced conduction produced by the induced charge. With $V_d = 0$, the decay of the charging current

was observed, and we found that the charging current became negligible compared with the true field-effect signal within five seconds after the step voltage was applied. Therefore, the true field-effect signal was accessible to measurement five seconds after the gate voltage was applied.

The decay of the field-effect signal was exponential in each case. The time constant of the decaying signal was between 10 and 20 sec and depended on which ambient gas was used. The field-effect signal at the time the fast surface states were in equilibrium with the induced charge (but before the interaction between the induced charge and the slow surface states became appreciable) was determined by extrapolating along the exponential field-effect signal curve to $t = 0$ as indicated in Fig. 3. The data for the curves of $(\Delta G)_{\text{expt}}$ vs. Q_{ind} for vacuum ambient shown in Fig. 4 were obtained in this manner.

5. ANALYSIS

The curves of $(\Delta G)_{\text{expt}}$ vs. Q_{ind} were com-

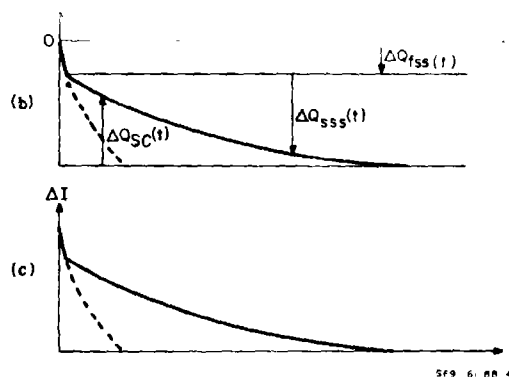


Fig. 3. Field-effect transients. (a) The gate-to-source voltage vs. time. (b) The induced charge vs. time. (c) The drain current vs. time. The broken line indicates the effect of the fast surface states.

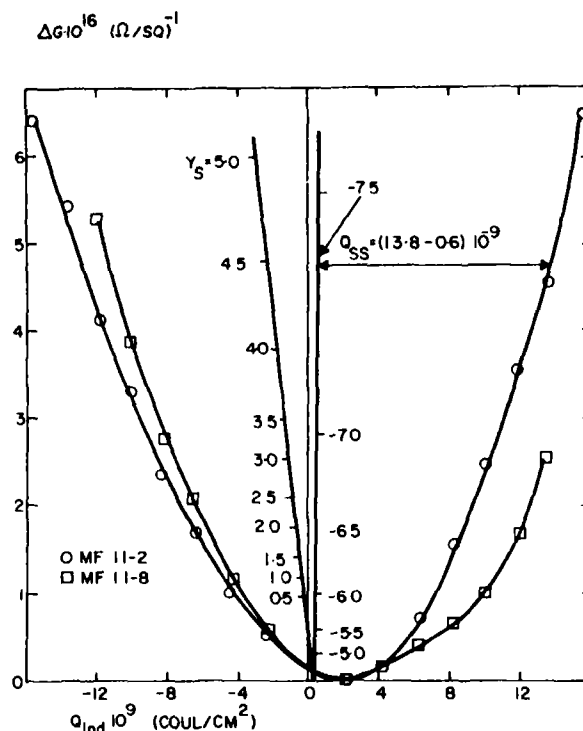


Fig. 4. The change in surface conductance vs. induced charge for a vacuum ambient of 5×10^{-9} torr.

puted from equations (10) and (11) by a computer program as discussed previously. The values of the bulk parameters n_i , n_b , N_m , and φ_m were determined from measurements of the ohmic current and the spacecharge-limited current in the x^+ -direction as described in Refs. [7] and [8]. The curves of $\Sigma_{ss} = Q_{ss}/e$ vs. y_s were obtained from the ΔG vs. Q_{ind} curves as discussed in Ref. [2].

(a) Surface-state parameters

Surface states are classified as either acceptor-type or donor-type. The normalized charge per unit area in acceptor-type surface states at an energy E_{ss}^A is given by equation (19)

$$\Sigma_{ss}^A = Q_{ss}^A/e = -N_{ss}^A/[1 + \exp(-y_s + w_{ss}^A)], \quad (19)$$

where N_{ss}^A is the number of acceptor type surface states per unit area at an energy E_{ss}^A and

$$w_{ss}^A = (E_{ss}^A - E_F)/kT + \ln(1/2). \quad (20)$$

The normalized charge per unit area in donor-type surface states at an energy E_{ss}^D is

$$\Sigma_{ss}^D = Q_{ss}^D/e = N_{ss}^D/[1 + \exp(y_s - w_{ss}^D)], \quad (21)$$

where N_{ss}^D is the number of donor-type surface states per unit area at an energy E_{ss}^D and

$$w_{ss}^D = (E_{ss}^D - E_F)/kT - \ln(2). \quad (22)$$

The surface-state parameters E_{ss} and N_{ss} are determined by fitting the curves of Σ_{ss} vs. y_s

by curves of the form of equations (19) and (21) as shown for vacuum ambient in Fig. 5. The results for vacuum, hydrogen, and oxygen ambients are summarized in Table 1. Due to

the large density of surface states and localized bulk states, the surface potential could not be practically varied by more than ± 0.23 eV (~ 10 kT). Most of the variation in the occupation probability occurs for y_s within ± 0.077 eV (~ 3 kT) of the energy of the state. Thus, surface states more than 0.3 eV above or below midgap could be present in the crystals without being detected by our measurements.

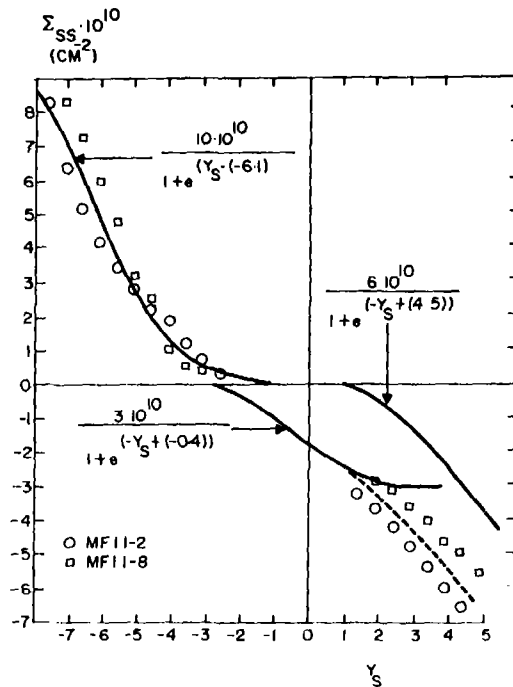


Fig. 5. The dimensionless charge in fast surface states vs. dimensionless surface potential for vacuum ambient.

Table 1. Surface-state parameters determined from field-effect measurements on metal-free phthalocyanine crystals

Ambient	Surface state type	density (cm^{-2})	Energy with respect to midgap (eV)
Vacuum	Donor	$1.0 \cdot 10^{11}$	-0.094
	Acceptor	$0.3 \cdot 10^{11}$	+0.052
Oxygen	Donor	$0.6 \cdot 10^{11}$	+0.170
	Acceptor	$1.2 \cdot 10^{11}$	-0.161
Hydrogen	Donor	$0.05 \cdot 10^{11}$	-0.104
	Acceptor	$0.8 \cdot 10^{11}$	+0.146
	Donor	$0.8 \cdot 10^{11}$	-0.044
	Acceptor	$0.6 \cdot 10^{11}$	+0.140

(b) Band bending at the surface

The shape of the bands at the surface is controlled by bulk parameters and can be calculated by performing the integration indicated in equation (12). The results of this calculation for the vacuum ambient are shown in Fig. 6. The upper branch of the curve corresponds to the bands bending upward at the surface; i.e. $y_s \leq 0$. The lower branch corresponds to the bands bending downward at the surface. In our experiments, the bands could not be bent by more than 10 kT by the transverse field; therefore we show the band

region

and $\leq 21 \times 10^{-3}$ cm thick for $y_s \sim 0$. In either case the space-charge region is sufficiently thin for the effects of surface states to be confined to the surface; i.e. a true bulk region exists which is approximately equal to the geometrical thickness of the crystal.

(c) Contact effects

In the preceding sections it was tacitly assumed that the measurement of the change in conductance between the end contacts represented the true change in surface conductance. For this to be true, one of the following conditions must be true: either (1) the end contacts are ohmic to the channel

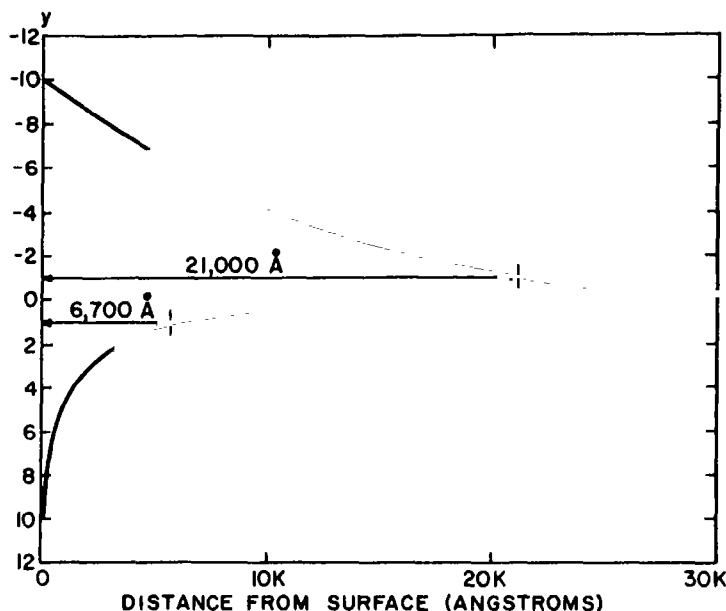


Fig. 6. Curves showing the band bending at the surface for $|y| \leq 10$. The upper branch corresponds to the bands bending upward, and the lower branch corresponds to the bands bending downward. The calculations were performed using data for vacuum ambient.

as well as to the bulk, or (2) there is good communication between the channel and the bulk. Since end contacts are usually chosen so that they are ohmic to the bulk, they are also ohmic to accumulation layers in the channel. However, they are not ohmic, on a d.c. basis, to inversion layers in the channel.

From injection experiments, it is known that evaporated gold contacts on metal-free phthalocyanine are ohmic to electron flow. Thus, for a channel in which the density of mobile electrons is much greater than the density of mobile holes, condition (1) is satisfied. Thus, there is no question about the interpretation of the field-effect data for $V_g > 0$. The case for $V_g < 0$ was considered in detail. Based on the analysis given in Ref. [12], our calculations indicate that the degree of communication between the bulk and the surface for $V_g < 0$ is good. Furthermore, because the gate electrode covers the entire

region of the crystal surface including the region near the end contacts, condition (1) may also be satisfied for $V_g < 0$. Suppose that a negative step voltage is applied to the gate bending the bands upward at the surface. With the bands bent upward at the surface, the diffusion of holes from the metal to the semiconductor is more probable. As time goes on, the holes induced into the channel fall into slow surface states, and the bands return to their original configuration. Thus, on a transient basis, the contacts may be ohmic to hole flow for the particular field-effect configuration used. Harrick[13] observed similar effects in his studies of metal-semiconductor contacts on nearly intrinsic germanium.

6. CONCLUSIONS

We believe that this paper reports the first precise determination of the surface-state parameters of metal-free phthalocyanine,

and together with Ref. [8] this paper characterizes the bulk and surface properties of metal-free phthalocyanine crystals. Our specific conclusions regarding surface properties are as follows: (1) There are at least 10^{11} cm^{-2} slow surface states on metal-free phthalocyanine crystals. The time constants of these states depend on the ambient gas. (2) There are three sets of fast surface states having densities of the order of 10^{11} cm^{-2} within 0.17 eV of midgap. The parameters of these states are not affected appreciably by oxygen or hydrogen ambients. Due to the location of these states near the center of the forbidden gap, they probably communicate with both bands and are therefore important in surface recombination processes. (3) Because of the very large density of localized bulk states, 90 per cent of the band bending occurs within about 10^{-4} cm of the surface; therefore, the effects of surface states are confined to the surface.

Acknowledgements—We would like to acknowledge that one of us (D.F.B.) was supported by the Westinghouse Solid State Doctoral Program. We thank Dr. P. M. P.

of the Westinghouse Aerospace and Electronics Systems Division for providing the vacuum pump used in our work.

REFERENCES

1. FRANKL D. R., *Electrical Properties of Semiconductor Surfaces*, Pergamon Press, Oxford (1967).
2. BROWN W. I., *Phys. Rev.* **100**, 590 (1955).
3. HEIL MEIER G. H. and ZANONI L. A., *J. Phys. Chem. Solids* **25**, 603 (1964).
4. BAESSLER H. and VAUBEI G., *Phys. Rev. Lett.* **21**, 615 (1968).
5. USOV N. N. and BENDERSKII V. A., *Sov. Phys. Semicond.* **2**, 580 (1968).
6. BARBE D. F. and WESTGATE C. R., *Bull. Am. phys. Soc.* **13**, 1479 (1968).
7. BARBE D. F. and WESTGATE C. R., *Solid State Commun.* **7**, 563 (1969).
8. BARBE D. F. and WESTGATE C. R., *J. chem. Phys.* **52**, 4046 (1970).
9. BARBE D. F., *Bulk and Surface Conduction in Metal-Free Phthalocyanine*, p. 110. Ph.D. dissertation, Dept. of Electrical Engineering, the John Hopkins University, 1969).
10. BARBE D. F., *The Field Effect in Crystals Having Large Densities of Localized States*. Submitted to the IEEE Transactions on Electron Devices.
11. WESTGATE C. R. and WARFIELD G., *J. chem. Phys.* **46**, 537 (1967).
12. MANY A., GOLDSSTEIN Y. and GROVER N. B., *Semiconductor Surface Science*, Vol. 2, North-Holland, Amsterdam, 1968.

IMPROVED DEBYE-WALLER FACTORS FOR SOME ALKALI HALIDES

JOHN S. REID and T. SMITH

Department of Natural Philosophy, The University, Aberdeen. AB9 2UF, Scotland

(Received 15 January 1970; in revised form 9 March 1970)

Abstract—Calculated Debye–Waller B_k factors are tabulated for the alkali halides NaF, NaCl, NaBr, NaI, KCl, KBr in the temperature range 5 to 295°K. The calculations were made by sampling eigen-data given by fitted shell models at 64,000 points in the Brillouin zone. Errors introduced by this sampling are shown, and the effect of the quasiharmonic frequency changes and the zero-phonon terms is discussed in detail. The high and low temperature limits of the Debye Temperature Θ_D , and several associated thermodynamic quantities for the sodium halides are also given. A comparison with experimental values indicates that there is not yet an entirely satisfactory agreement with the calculations.

INTRODUCTION

FOR six alkali halides Buyers and Smith[1] have discussed the Debye–Waller factors calculated from the force models of Karo and Hardy[2], and concluded that these values were likely to be more reliable than the experimentally determined factors. However, since the appearance of this article, shell model parameters have been fitted to the measured dispersion curves of all the materials considered. It has been confirmed from the measured dispersion curves that force models such as [2], which are determined only by elastic and i.r. data, can be seriously in error near the zone boundary. Hence we have now made use of the fitted shell models to derive the Debye–Waller factors. Also, the summations can be performed with a much finer mesh covering the Brillouin zone and the accuracy of the calculational technique can thus be more easily investigated. With these improvements we have calculated a more accurate set of Debye–Waller factors for NaF, NaCl, NaBr, NaI, KCl and KBr.

In Section 1 the calculation is briefly discussed and a method of extrapolating the quasiharmonic frequencies to lower temperatures is given. In Section 2 the results are tabulated and a comparison made with some experimental observations.

1. CALCULATION

We shall use the method of Buyers and Smith[1] and discuss only two refinements which improved the accuracy of the calculation. Our notation and a summary of formulae is given in the Appendix.

For calculations over a wide range of temperature

to Θ_D we use the shell model dispersion curves to Θ_D but an overestimate near 0 K. Our correction procedure assumes that at temperatures below room temperature

$$\Delta\omega_{\mathbf{q}} \approx \left(\frac{\partial\omega_{\mathbf{q}}}{\partial v} \right)_T \Delta v \quad (1)$$

giving

$$\frac{\Delta\omega_{\mathbf{q}}}{\omega_{\mathbf{q}}} \approx -\gamma_{\mathbf{q}} \frac{\Delta v}{v} \quad (2)$$

$$= -3\alpha(T)\gamma_{\mathbf{q}}(T) \quad (3)$$

where $\alpha(T)$ is the linear expansion coefficient. The Gruneisen parameters $\gamma_{\mathbf{q}}(T)$ for each

mode are unknown, but since we wish to calculate a weighted average over all the modes ($\mathbf{q}j$) it is satisfactory to represent the change in frequencies by a mean $\bar{\gamma}(T)$ which produces the correct change in the weighted average. Following Pautamo[4] we choose the temperature dependent

$$\bar{\gamma}(T) = \gamma_0 + (\gamma_{295} - \gamma_0)C_r(T)/3.4k \quad (4)$$

giving

$$\frac{\Delta\omega(T)}{\omega(295)} = -3 \int_T^{295} \left(\gamma_0 + (\gamma_{295} - \gamma_0) \frac{C_r(\tau)}{3.4k} \right) \alpha(\tau) d\tau \quad (5)$$

where the high and low temperature Gruneisen

constants γ_{295} and γ_0 are obtained from thermodynamic measurements or estimates[4]. In practice the results are not sensitive to γ_0 since $\alpha(T)$ is small at low temperatures. The specific heat $C_r(T)$ was calculated from the shell models with the correction (5) made at each temperature, and Fig. 1 shows the equivalent Debye temperatures $\Theta^D(T)$ for the sodium halides. The size of the frequency changes is given in Fig. 2(a) and the effect on the Debye-Waller B_k values of ignoring these can be seen for NaBr in Fig. 2(b). It is clearly desirable to incorporate some frequency corrections.

The sampling necessary to evaluate B_k (equation (3a)) was carried out with a bcc

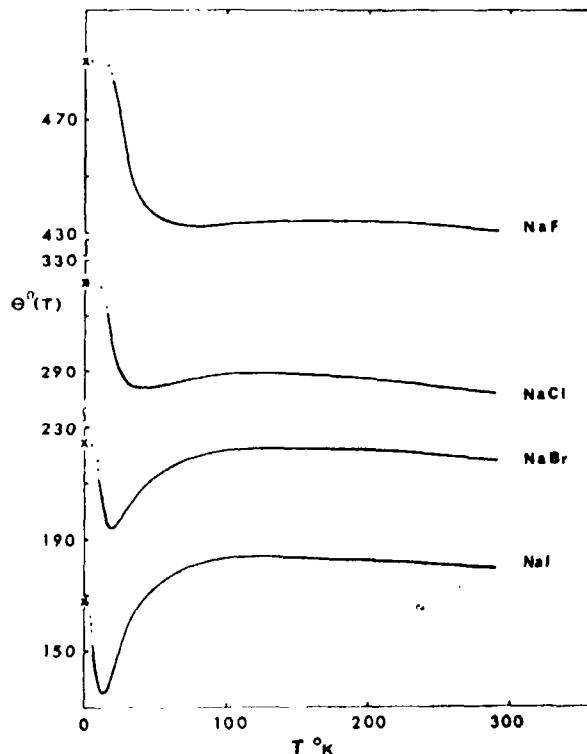


Fig. 1 Values for the sodium halides of the specific heat Debye temperature $\Theta^D(T)$ calculated from the models with the quasiharmonic frequency changes of equation (5). The crosses are the 0°K values of Lewis J. T., Lechoczky A. and Briscoe C. V., *Phys. Rev.* **161**, 877 (1967).

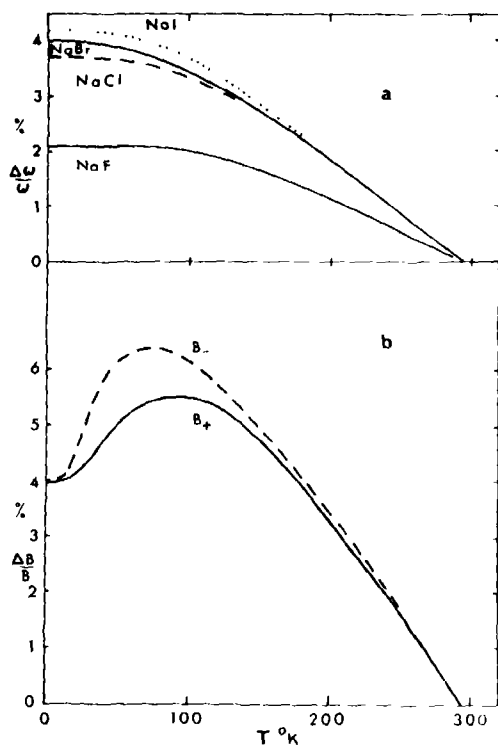


Fig. 2. (a) The percentage frequency changes given by equation (5) for the Sodium halides. (b) The percent change in the Debye-Waller B_k factors of NaBr when the frequencies at 295°K are used in place of the correct frequencies.

mesh of points covering the Brillouin zone, with n points along the [100] axis to the zone boundary. The number of mesh points (N) is therefore $(2n)^3$. Values of n between 3 and 20 were used. Because of the cubic symmetry, the sums were performed over only n_R sample points in the irreducible 1/48th of the Brillouin zone. Table 1 shows n_R for the range of mesh sizes of interest. As discussed in [1] it is necessary to treat the zerophonon region separately and the detailed assumptions made are the same as those used in a recent paper on the evaluation of the total phonon scattering cross-section (Reid J. S. and Smith T., *J. Phys. (C)*, to be published). The percentage contribution of this region is similar for all the materials

Table 1. The number of points (n_R), including the origin, in the reduced zone for a mesh of size n

Mesh size n	No. of irreducible points n_R	No. of points in zone N
3	16	216
4	30	512
5	48	1000
6	74	1728
8	149	4096
10	262	8000
12	422	13,824
16	913	32,768
20	1686	64,000
25	3143	125,000
30	5272	216,000
35	8184	343,000

and is shown for NaCl in Fig. 3(a) as a function of the sample size. Even for the largest sample of 64,000 wave vectors its value is 1.6 per cent at room temperature. Figure 3(b) shows the zerophonon variation with temperature for the sample

The parameters of the shell models used to generate the eigendata are shown in Table 2 in the notation of Woods *et al.* [5]. These models give frequencies at low temperatures for NaI (100°K) and KCl (115°K), and at 295°K for the other halides. The method in Section 1 was used to obtain the frequencies at other temperatures.

Table 3 gives the B_k values of the 6 materials for temperatures in steps of 20 deg from 295 to 5°K. A comparison with the B_k values of the deformation dipole models [1] shows substantial differences, with larger values now given for the heavy halides and smaller values for the light halides. The KCl values agree to

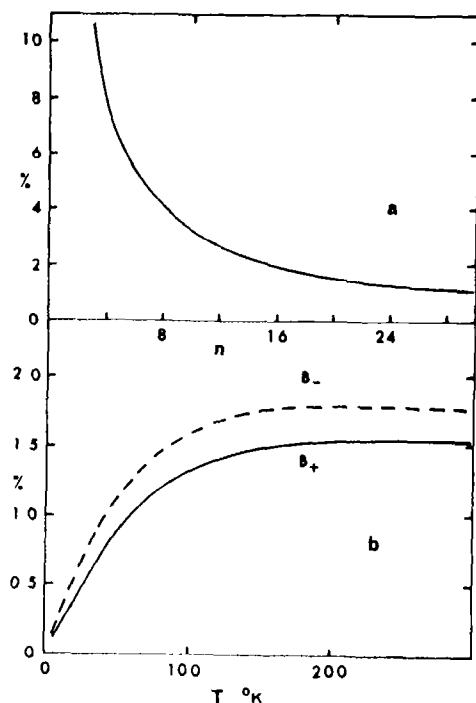


Fig. 3. The percentage contribution of the zero-phonon term to the B_k values of NaCl (a) at 295°K for different mesh sizes, where n is the number of points to the [100] zone boundary (b) Over the range of temperatures with the mesh $n = 20$.

within a few per cent but for the other materials there is an average discrepancy of about 10 per cent. Though the general trend is for the fitted shell models to give more widely separated factors than models determined by macroscopic data, inversion points (where Debye-Waller factors of the ions are equal) occur for both NaF (at 275°K) and KBr (at 75°K).

The errors in the tabulated values arise from errors in both the method of calculation and the experimental frequencies used to determine the models, and also from any inadequacy of the models. The accuracy of the calculational technique has been discussed in the previous section and it can be concluded that uncertainties caused by the finite mesh

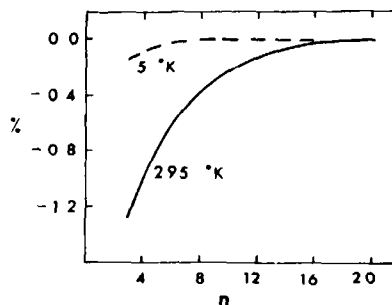


Fig. 4. The percentage change in the B values of NaCl from those calculated using the mesh with $n = 20$. (n can take integer values only.)

and the zero-phonon term amount to less than 0.1 per cent (Figs. 3 and 4). Also, a misestimation of the quasiharmonic frequency shift by 25 per cent would lead to a maximum change in the B_k factor of 1.2 per cent (Fig. 2). In addition, errors in B_k depend on the errors in the experimental frequencies, ω_i , through the factors $(\partial B_k / \partial \omega_i)^2$. The exact calculation of these terms for a given model is not feasible and hence we shall consider instead an upper limit to the standard deviation $\sigma(B_k)$. Even for the simpler factor $\bar{B}$, which does not depend on the eigenvectors, the error cannot be exactly calculated from the model frequencies (equation (9a)) since the errors in neighbouring values of ω_λ are strongly correlated. Therefore we shall take as the upper limit to the error in $\bar{B}$ the error which would occur if $\bar{B}$ were calculated directly from the experimental frequencies. This is a slowly varying function of temperature and is smallest at low temperatures but can be approximated over the whole range as

$$\frac{\sigma(\bar{B})}{\bar{B}} \approx \frac{1}{\sqrt{N_i}} \%$$

where there are N_i determining frequencies known to about 2 per cent. This procedure is reasonable since it is observed that all the models fit the experimental frequencies well, with a value of χ^2 (e.g. Table 2, Ref. [a]) near unity, and moreover systematic differences between the models and experimental values

Table 2. Parameters of the shell models fitted to measured phonon frequencies

Material	A ($e^2/2V$)	B ($e^2/2V$)	A'' ($e^2/2V$)	B'' ($e^2/2V$)	Z (e)	Y_1 (e)	k_1 (e^2/V)	Y (e)	k (e^2/V)
NaF ^[a]	9.26	-0.77	0.34	-0.02	0.907	-8.3895	6469.0	-1.8751	117.07
NaCl ^[b]	10.79	-1.146	0.4358	0.0055	1.0	0.0		-2.648	90.29
NaBr ^[c]	11.392	-1.0442	0.0	0.0	1.0	1.004	48.97	-3.604	166.8
NaI ^[d]	9.94	-0.86683	0.618	-0.041	0.89	2.2126	153.91	-3.9679	231.22
KCl ^[e]	12.12	-1.0228	-0.10	-0.058	0.918	11.267	4530.1	-2.917	232.78
KBr ^[f]	12.58	-1.11225	-0.526	-0.025	0.974	2.7077	231.36	-2.7435	159.77

[a] Model VI of BUYERS W. J. L., *Phys. Rev.* **153**, 923-930 (1967).[b] Fitted to the 300°K data of RAUNIO G., ALMQUIST L. and STEDMAN R., *Phys. Rev.* **178**, 1496-1499 (1969).[c] Model II of REID J. S., SMITH F. and BUYERS W. J. L., *Phys. Rev.* (To be published) (1970).[d] Model VI of COWLEY R. A., COCHRAN W., BROCKHOUSE B. N. and WOODS A. D. B., *Phys. Rev.* **131**, 1030-1039 (1963).[e] Model VI of COPILEY J. R. D., MACPHERSON R. W. and TIMUSK L., *Phys. Rev.* **182**, 965-972 (1969).

[f] Model VI parameters interpolated to 300°K from Ref. [d].

Table 3. The Debye-Waller B_k factors for NaF below 295°K. The values were calculated u_{Na}

Temperature °K	NaF		NaCl		NaBr	
	B_{Na}	B_F	B_{Na}	B_{Cl}	B_{Na}	B_{Br}
295.000	0.8685	0.8671	1.5565	1.3481	1.9710	1.8991
275.000	0.8121	0.8121	1.4464	1.2514	1.8294	1.4810
255.000	0.7569	0.7583	1.3389	1.1567	1.6910	1.3649
235.000	0.7029	0.7060	1.2338	1.0640	1.5555	1.2509
215.000	0.6504	0.6551	1.1313	0.9734	1.4232	1.1391
195.000	0.5993	0.6059	1.0313	0.8849	1.2942	1.0295
175.000	0.5501	0.5587	0.9344	0.7988	1.1688	0.9221
155.000	0.5030	0.5137	0.8409	0.7153	1.0473	0.8170
135.000	0.4584	0.4716	0.7514	0.6348	0.9302	0.7144
115.000	0.4170	0.4329	0.6668	0.5580	0.8187	0.6145
95.000	0.3799	0.3986	0.5884	0.4859	0.7142	0.5179
75.000	0.3483	0.3700	0.5187	0.4205	0.6198	0.4260
55.000	0.3240	0.3482	0.4614	0.3650	0.5401	0.3414
35.000	0.3084	0.3340	0.4213	0.3247	0.4816	0.2705
15.000	0.3008	0.3266	0.4016	0.3046	0.4492	0.2285
5.000	0.2994	0.3253	0.3982	0.3012	0.4432	0.2220

do not exist over large regions of the Brillouin zone. In general the least-squares fitting program used some 58 frequencies for all the materials except NaCl when only 8 were used. Hence the upper limit to the uncertainty in $\bar{B}$ due to the experimental frequencies is 0.2 per cent for all the materials except NaCl for which it is 0.4 per cent. For the B_k factors an additional source of error arises from the adequacy of the model through its ability to generate eigenvectors (equation (3a)). We have examined the numerical values of the eigenvectors from several different force models for the alkali halides and conclude that this is likely to contribute a standard deviation $\sigma(B_k)/(B_k)$ of 1.5 per cent. Thus we conclude that the B_k values have a maximum standard deviation of 2 per cent but the values of $\bar{B}$ and the relative B_k values at different temperatures are determined to 1.5 per cent.

A few calculations have already been made with the fitted shell models for KCl, KBr and NaI. Copley *et al.* (Table 2, Ref. [e]) have revised their values for KCl (private communication) and they are now in good agreement with Table 3. The 300°K values for NaI and KBr given by Pryor[6] are within a few per cent of those in Table 3 but no details of his zero-phonon term or frequency changes are given. The values for NaI and KBr in Table 3 lie half way between the harmonic and anharmonic values calculated by Cowley and Cowley[7]. This is encouraging since they estimated that their anharmonic contribution was too large by a factor of two. They also suggested that a harmonic model with no second neighbour force constants might give equal Debye-Waller factors at high temperatures. For NaBr this is not the case since the different harmonic B_k values at high temperature lie on different lines through $T = 0$, and at the melting point (755°K) the ratio of the harmonic factors, B_{Na}/B_{Br} , is 1.22. This ratio is increased when quasiharmonic frequency changes are included.

Raichenko's suggestion[8] that the sum of the root mean square displacements of the two

ions was a constant fraction of the lattice constant at the melting point was examined by evaluating $((3B_+/2)^{1/2} + (3B_-/2)^{1/2})/2\pi d$ at the melting point of each material (see equation (7a)). This was found to be nearly constant with a value 0.162 ± 0.004 for the different materials, indicating that the alkali halides melt when the vibrational amplitudes are about 8 per cent of the lattice constant.

We have not given values for the Debye-Waller factors above room temperature because they are easy to estimate fairly accurately but difficult to calculate exactly. In the harmonic approximation the B_k values vary linearly at high temperature and any curvature at 300°K can be estimated from the values given in [1]. An extrapolation of the frequency changes of Fig. 2 gives a T^2 correction which increases the B_k values, but even in the quasiharmonic approximation terms not included in equation (1) are important. To obtain the correct temperature dependence a detailed anharmonic calculation appears to be essential (e.g. Cowley and Cowley[7], Wolfe and Goodman[9] although substantial progress can be made with simpler models (e.g. Willis[10], Dash *et al.*[11]).

It is widely recognised that a comparison with experimental results is difficult because of the spread in the experimental B_k values for one material. The uncertainties involved with conventional X-ray measurements have been discussed by several authors (e.g. [12-18]). Amongst other factors, the B_k determinations are particularly sensitive to diffuse scatter near Bragg peaks and only recently has it been possible to accurately investigate this scatter [19] and to make a calculation of the multiphonon contribution (Reid J. S. and Smith T., *J. Phys. (C)*, to be published). Also, Jennings [20], has pointed out that earlier experiments did not include a measurement of the polarization of the X-ray beam. However, an extensive set of measurements on NaCl (Merisalo and Paakkari[15], Mansikka and Kulmala[16], Linkoaho[17]) has produced values at 300°K which are 20 per cent higher than those of

Table 3, and there is a similar discrepancy for the NaF values, [13] and [16]. But the uncertainty in the experimental values is also not clear, for a recent set of measurements of B_{Na} and B_{Cl} over a wide range of temperatures (B. Larson and C. W. Tompson, private communication) are in better agreement with Table 3 though lying below these values. The uncertainties in the calculation appear to be much less than these differences. The non spherical distortion of the charge distribution in the crystal (Mansikka[16], and Kurki-Suonio and Meisalo[18]) produces effects which are an order of magnitude too small.

Values found from neutron scattering experiments (e.g. Pryor[6], Myers *et al.*[21]), are not sufficiently accurate to distinguish between the values of Table 3 and those predicted by the *DD* model[1]. However, the Mössbauer experiment on NaI of Hafemeister *et al.*[22] gives directly the 80°K value for $B_{1122} = 0.53 \pm 0.07$ which is in better agreement with the calculation value of $B_{1122} = 0.574$ than with the *DD* value of 0.619.

The Debye temperature Θ^W used by several authors (e.g. [21], [23] and [24]) is related to the mean B value (vid. Appendix), and also to

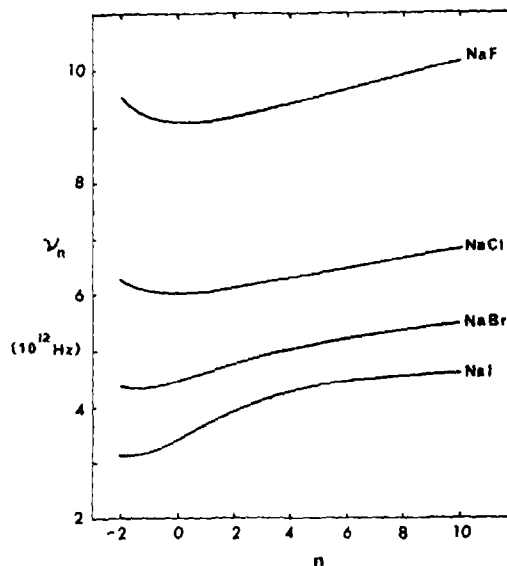


Fig. 5 The reduced moments ν_n (equation (6)) for the sodium halides.

the Θ^W

Table 4. Low and high temperature Debye-Waller factors, Θ^W , and first and second negative moments of the modified charge distribution at 5°K are compared with experiment. The units of μ_n are $(10^{13} \text{ rad./sec})^{-n}$.

	Θ_0^W	Θ_x^W	Θ_z^W	μ_1	μ_2
	[a]	[b]	[c]	[d]	
NaF	440	448	431	0.260	0.0837
NaCl	290	291	283	0.395 (-2.0%)	0.192 (-7.7%)
NaBr	207	202	219	0.553	0.396
NaI	154	143	181	0.746 (1.6%)	0.781 (+1.7%)
KCl	223	219	223	0.513 (1.0%)	0.343 (-0.9%)
KBr	163	156	177	0.702 (4.0%)	0.673 (6.3%)

[a] $k\Theta_0^W = h\nu_1(5^\circ\text{K})$, where the reduced moment ν_1 has been evaluated for the modified distribution at 5°K.

[b] $k\Theta_x^W = h\nu_x(295^\circ\text{K})$

[c] $k\Theta_z^W = h\nu_z(295^\circ\text{K})$.

[d] The figures in brackets are the percentage deviation of the calculated values given from the experimental values[1].

where the moments (μ_n) of the distribution $g(\omega)$ are given by

$$\mu_n = \int \omega^n g(\omega) d\omega / \int g(\omega) d\omega.$$

The reduced moments are of general interest and can be seen in Fig. 5. Values for the low and high temperature limits of Θ^w are given in Table 4 along with values of μ_{-1} and μ_{-2} which are compared with experimental values obtained from specific heat measurements. The discrepancies of a few per cent are not unreasonable since the models were fitted to measurements made in the zero sound regime [25] and hence the quasiharmonic frequencies are different from those relevant to thermodynamic measurements.

Acknowledgements—We would like to thank Dr M. J. L. Sangster for supplying most of the routines necessary to calculate eigendata on an arbitrary mesh. The calculations were performed on the Atlas computer of the Science Research Council.

REFERENCES

- BUYERS W. J. I. and SMITH I., *J. Phys. Chem. Solids* **29**, 1051–1057 (1968).
- KARO A. M. and HARDY J. R., *Phys. Rev.* **129**, 2024 (1963).
- BUYERS W. J. I. and SMITH I., *J. Phys. Chem. Solids* **25**, 483–486 (1964).
- PAULAMO Y., *Ann. Acad. Sci. Fenn. A129*, 1–45 (1963).
- WOODS A. D. B., COCHRAN W. and BROCKHOUSE B. N., *Phys. Rev.* **119**, 980–999 (1960).
- PRYOR A. W., *Acta crystallogr.* **20**, 138–140 (1966).
- COWLEY F. R. and COWLEY R. A., *Proc. R. Soc. A292*, 209 (1966).
- RAICHENKO A. I., *Soviet Phys. solid State* **5**, 1447 (1964).
- WOLFE G. A. and GOODMAN B., *Phys. Rev.* **178**, 1171–1189 (1969).
- WILLIS B. I. M., *Acta crystallogr.* **A25**, 277–300 (1969).
- DASH J. G., JOHNSON D. P. and VISSCHER W. M., *Phys. Rev.* **168**, 1087–1094 (1968).
- SUORTTI P., *Ann. Acad. Sci. Fenn. A240*, 1 (1967).
- MERISALO M. and MEISALO V., *Ann. Acad. Sci. Fenn. A211*, 1 (1966).
- MEISALO V. and INKINEN O., *Acta crystallogr.* **22**, 58 (1967).
- MERISALO M. and PAAKKARI I., *Acta crystallogr.* **23**, 1107–1109 (1967).
- MANSIKKA K. and KULMALA V., *Ann. Acad. Sci. Fenn. A269*, 1–15 (1967).
- LINKOAHU M., *Ann. Acad. Sci. Fenn. A284*, 1–31 (1968).
- KURKI-SUONIO K. and MEISALO V., *Ann. Acad. Sci. Fenn. A241*, 1–16 (1967).
- 8th Crystallography Conference, *Acta crystallogr.* **A25**, S14–S34 (1969).
- JENNINGS L. D., *Acta crystallogr.* **A24**, 472–474 (1968).
- MYERS W. R., BENNION R. B. and BRUGGER B. M., *Acta crystallogr.* **A25**, S30 (1969) (abstract only).
- HAFEMEISTER D. W., DE PASQUALE G. and DE WAARD H., *Phys. Rev.* **135**, B1089–1101 (1965).
- BALDWIN T. O., PEARMAN G. T. and TOMPSON C. W., *J. Phys. Chem. Solids* **26**, 303–306 (1965).
- YATES B., *Phil. Mag.* **14**, 179–184 (1966).
- COWLEY R. A., *Proc. Phys. Soc.* **90**, 1127–1147 (1967).
- MARADUDIN A. A., MONTROLL F. W. and WEISS G. H., *Solid State Physics*, Suppl. 3, pp 5–65 Academic Press, New York (1963).

APPENDIX

The Debye-Waller term for the k th atom in the unit cell is

$$e^{-W_k} \quad (1a)$$

where

$$W_k = B_k \sin^2 \theta / \lambda^2 \quad (2a)$$

and

$$B_k = \frac{8\pi^2}{3} \frac{1}{2N} \sum_{\mathbf{q}} \left(\frac{E}{\omega_{\mathbf{q}}} \right) \left| \frac{\epsilon(k/\mathbf{q})}{m_k^{1/2}} \right|^2. \quad (3a)$$

The calculated quantities B_k depend on the mean energy of a mode ($\mathbf{q}$) of frequency $\omega_{\mathbf{q}}$

$$E_{\mathbf{q}} = \hbar \omega_{\mathbf{q}} (1/(\exp(\hbar \omega_{\mathbf{q}}/kT) - 1) + \frac{1}{2}) \quad (4a)$$

$$= \hbar \omega_{\mathbf{q}} (n(\omega) + \frac{1}{2}) \quad (5a)$$

and on the eigenvectors $\epsilon(k/\mathbf{q})$ appearing in the normal co-ordinate transformation

$$u(k) = \frac{1}{N} \sum_{\mathbf{q}} \frac{\epsilon(k/\mathbf{q})}{m_k^{1/2}} e^{i\mathbf{q} \cdot \mathbf{r}(k)} Q(\mathbf{q}) \quad (6a)$$

(Maradudin *et al.* [26]). The mean square amplitude

$$\langle u(k) \rangle = 3B_k/8\pi \quad (7a)$$

and a mean $\bar{B}$, independent of the eigenvectors, is defined as

$$\bar{B} = \sum_k m_k B_k / \sum_k m_k \quad (8a)$$

$$= \frac{8\pi^2}{3} \frac{1}{2N} \sum_{\mathbf{q}} \left(\frac{E}{\omega_{\mathbf{q}}} \right) \quad (9a)$$

With g atoms/unit cell, $\bar{B}$ is given in terms of the Debye temperature Θ^w as

$$\bar{B} = \frac{2gh^2}{\bar{m}} \cdot \frac{3T^2}{k(\Theta^w)^3} \left[\int_0^{x_m} \frac{x \, dx}{e^x - 1} + \frac{x_m^2}{2} \right] \quad (10a)$$

At low temperatures this reduces to

where

$$x_m = \Theta^w/T \quad (11a)$$

$$\bar{m} = \sum_k m_k/g \quad (12a)$$

$$\bar{B} \approx \frac{3gh^2}{2mk\Theta^w}. \quad (13a)$$

ORBACH TYPE REORIENTATION PROCESSES IN THE PARAELASTIC RELAXATION OF O_2^- IN KCl

G. PFISTER* and M. BÖSCH

Laboratory of Solid State Physics, Swiss Federal Institute of Technology, Zürich, Switzerland

(Received 10 February 1970)

Abstract—In the reorientation of O_2^- molecule ions in KCl under uniaxial stress a process occurs which can be regarded as an Orbach type process. A detailed experimental study of this process has been performed. The results are discussed in terms of rate equations and of the one phonon transition probability derived by Gosar and Pirc. The theoretical predictions are in excellent agreement with the experimental results. From the analysis the effective tunneling matrix elements, the effective moments of inertia and the potential barrier for the rotation by 90° are obtained.

1. INTRODUCTION

IN A PREVIOUS paper [1], hereafter referred to as I, we presented a detailed study of the stress and temperature dependence of the paraelastic relaxation of O_2^- molecule ions in the host lattices KCl, KBr and KJ. In most of these experiments the stress was chosen along the [001]—and [111]—axes, and the effect of the isotropic substitution of $^{18}O_2^-$ for $^{16}O_2^-$ on the paraelastic relaxation rate has been studied. For certain stress axes a reorientation process was found in KCl and KBr which is an analogue of the Orbach process [2], known from spinlattice relaxation. The molecules do not reorient *directly* into the level with the lowest energy, but *indirectly* by two consecutive rotations by 60° through an intermediate orientational level with a higher energy. The occurrence of an Orbach type reorientation process in the paraelastic relaxation of the O_2^- molecules in alkali halides has first been suggested by Silsbee [3], who also performed the first experiments along this line.

The present paper contains a detailed study of the Orbach processes in KCl. It should be read in conjunction with the previous paper I.

2. PREPARATION OF THE SAMPLES

The paraelastic relaxation times discussed in this paper were determined from the time

*Present address: Xerox Corporation, Rochester, New York, 14603, U.S.A.

dependence of the population difference measured by means of EPR of two nearly degenerate orientational levels. In order to obtain a reasonable signal to noise ratio in the corresponding change of the EPR signal, the crystals had to be doped with a higher O_2^- concentration than can be reached by simply annealing them in a dry oxygen atmosphere [1,3,5]. The following method permitted to increase the oxygen concentration by about a factor

$$c + O_2 \xrightarrow{\text{annealing}} c + O_2^-$$

a surface layer with a very high oxygen concentration is formed. The oxygen diffuses then slowly into the bulk until after a few days a homogenous concentration is reached. It was verified that the experimental results do not depend upon the method of the doping and upon the O_2^- concentration, which was of the order of 10^{18} cm^{-3} .

3. EXPERIMENTAL RESULTS AND THEIR INTERPRETATION

In all the experiments reported here the uniaxial stress was applied along the axis lying in the (110)-plane and forming an angle θ with

the [001]-direction of the cubic cell. The measurements were made for three stress axes characterized by $\theta = 10^\circ$, 21° and 30° . By symmetry the stress splits the sixfold degenerate orientational groundstate into the four levels *a*, *b*, *c* and *d* shown in Fig. 1. In our experiments the energy splittings of the different levels were typically in the range 0.1–2.0°K for U_{bu} , 3 and 10°K for U_{ca} and 5 and 15°K for U_{da} . As indicated in Fig. 1 the

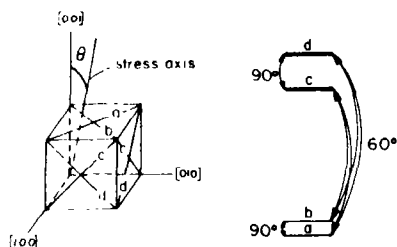


Fig. 1. Level scheme underlying the discussed experiments. The stress axis is in the (110)-plane and forms the angle θ with the [001]-direction of the cubic unit cell. θ was chosen to be 10° , 21° and 30° .

rotation of a molecule by 90° is equivalent to a direct transition from the level *d* or *b* to the level *c* or *a*, respectively. The remaining transitions correspond to rotations by 60° .

Figure 2 shows an example of the recorded time dependence of the four populations after the application of a stress along the axis $\theta = 21^\circ$ at $t = 0$. Initially one observes a fast reorientation of the molecules. The population of the two lower lying levels *a* and *b* increases at the expense of the two higher lying levels. After a time t_0 of the order of some seconds the levels *c* and *d* are nearly emptied and for $t > t_0$ no further change in their populations is observed. On the other hand, the populations of the levels *a* and *b* change at a very slow rate of the order of $100 \cdot t_0$. The population of level *a* further increases whereas the population of level *b* decreases, both according to a single exponential function with the same time constant τ_3 .

These experimental results can be interpreted along the lines suggested by Silsbee[3].

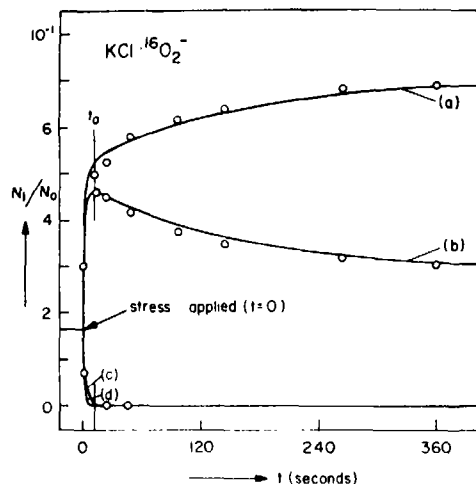


Fig. 2. Time dependence of the population of the four levels *a*, *b*, *c* and *d* of sample No. 3 after the application of the uniaxial stress $1.92 \cdot 10^8$ dyn/cm² at $T = 1.52^\circ\text{K}$ along the axis $\theta = 21^\circ$. The curves were calculated using the two fitted parameters τ_1' and τ_2' listed in Table 2(a). The points are taken from experimental recordings.

The initial fast rise (decay) of the populations of the levels *a* and *b* (*c* and *d*) is due to reorientations by 60° of molecules initially in the levels *c* and *d* into the levels *a* and *b*. One thus expects the relaxation rates describing the time behaviour of the system for $t < t_0$ to be of the same order of magnitude as the relaxation rates for stress along [001] or [111]. Furthermore they should qualitatively show the same stress and temperature dependence as $1/\tau_{001}$, i.e. the rates should increase with increasing stress and for not too high stresses they should be proportional to the temperature. This is in fact observed. As will be shown in the next paragraph the initial time dependence of the four populations can be approximated by two exponential functions with the time constants τ_1 and τ_2 . One relaxation rate, $1/\tau_1$, predominantly characterizes reorientations of molecules from level *d*, the other, $1/\tau_2$, reorientations of molecules from level *c* into the lower lying levels *a* and *b*. Since τ_1 corresponds to a larger energy difference one has $\tau_1 < \tau_2$. However, the accuracy of the experi-

ment was not sufficient to separate the two relaxation times τ_1 and τ_2 for a detailed investigation.

As is shown in Figs. 3–5 the low relaxation rate $1/\tau_3$ describing the relaxation behaviour of the system for $t > t_0$ shows a completely different stress and temperature dependence than do $1/\tau_{001}$ and $1/\tau_{111}$ [1,3]. At *constant temperature* the rate decreases with increasing stress and finally reaches a stress independent value. This value turns out to be proportional to the temperature. At *constant stress* $1/\tau_3$ falls off exponentially with decreasing temperature and finally bends over into a linear dependence on temperature (Fig. 5).

The nearly equal population of the lower levels a and b at $t = t_0$ indicates that the probability for the 90° rotation $b \rightarrow a$ is much smaller than the probability for the

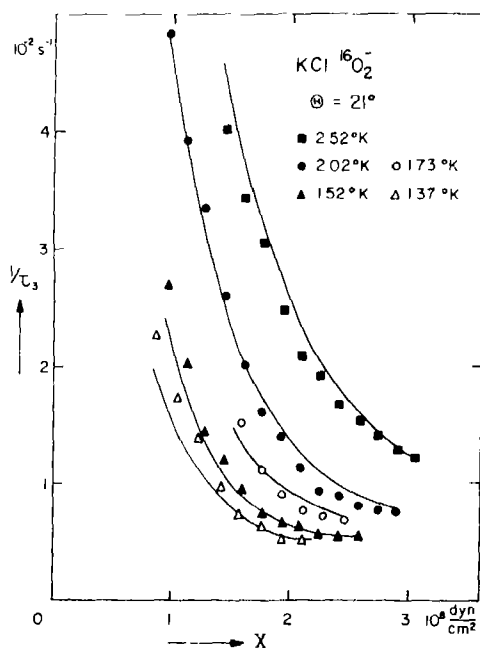


Fig. 3. Stress dependence of $1/\tau_3$ at various temperatures for two KCl: $^{16}\text{O}_2^-$ samples: No. 3 (■ ● ▲) and No. 4 (○ △). The stress was applied along the axis $\theta = 21^\circ$. The theoretical curves were calculated with the parameters pertaining to these samples and given in Table 2(a).

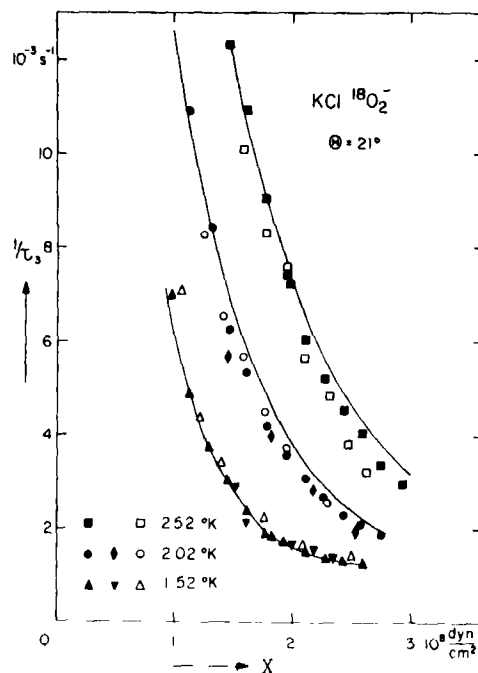


Fig. 4. Stress dependence of $1/\tau_3$ at various temperatures for two KCl: $^{18}\text{O}_2^-$ samples: No. 3 (■ ● ▲) and No. 4 (○ △).

eqt.

the rate $1/\tau_3$ involves transitions predominantly between the levels a and b . Two different processes can contribute to these:

(a) Direct transition

The molecules reorient *directly* by the 90° rotation $b \rightarrow a$. Since the levels a and b have equal degeneracy, the relaxation rate for the direct transition $b \rightarrow a$ should increase with increasing stress as has been observed for stress along [111]. However, this change is too small to be detected in these experiments since $U_{ba} < kT$ (see Figs. 3(c), 3(d) and 4(c), 4(d) of I).

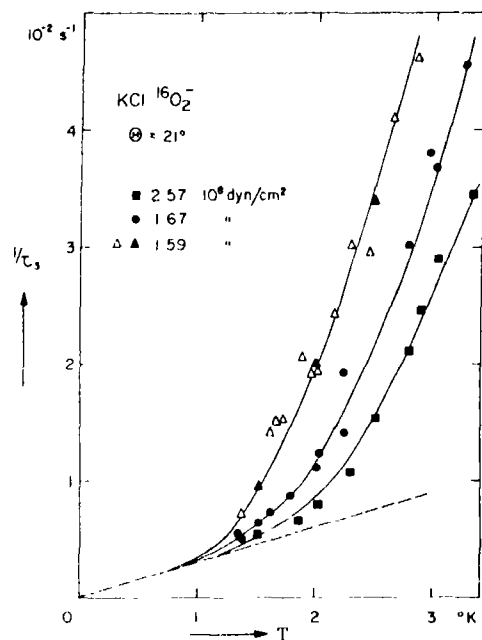


Fig. 5. Temperature dependence of $1/\tau_3$ at different loadings along the axis $\theta = 21^\circ$ for three different KCl. $^{16}\text{O}_2^-$ samples: No. 3 (■), No. 4 (Δ) and No. 5 (●). The theoretical curves were calculated using the parameters given in Table 2(a).

(b) Orbach process

The molecules reorient *indirectly* by two consecutive rotations by 60° through an intermediate higher lying level *c* or *d*. Since the first rotation involves an absorption of phonons the probability of the Orbach process falls off exponentially with increasing excitation energy, i.e. with increasing stress.

In KCl the tunneling matrix elements are an order of magnitude larger for the 60° rotations than for the 90° rotations [1]. This fact explains the observed stress and temperature dependence of $1/\tau_3$. For small stresses and not too low temperatures the Orbach process is dominant. With increasing stress or decreasing temperature this process dies out until finally the direct 90° rotation dominates. The proportionality between relaxation rate and temperature at high stresses indicates that the 90° rotation is a one phonon process, a result

which has also been observed for the 60° rotation [1,3,5].

4. EVALUATION OF THE RELAXATION RATES

$1/\tau_1$, $1/\tau_2$ AND $1/\tau_3$

(a) The application of the rate equations

The stress-induced splitting of the orientational energy levels can be computed from the relations given in 1. For the stress axes used in the present experiments one obtains for the splittings per unit stress

$$\begin{aligned} U_b - U_a &= \frac{1}{2}(b_1 - b_3)s_{44}\sin^2\theta \\ U_{d(c)} - U_a &= [b_2 - \frac{1}{2}(b_1 + b_3)](s_{12} - s_{11}) \\ &\quad \times (\frac{1}{2}\sin^2\theta - \cos^2\theta) + \frac{1}{2}(b_1 - b_3)s_{44}\frac{1}{\sqrt{2}}\sin\theta \\ &\quad \times (1/\sqrt{2}\sin\theta_{12}^+ \cos\theta) \end{aligned} \quad (1)$$

θ is the angle between the stress axis and the [001]-direction of the cubic crystal, s_{ij} are the elastic compliances and b_j the measured coupling coefficients [5] (components of the elastic dipole).

We assume that there is no correlation between subsequent rotational jumps of a given molecule. The populations N_j of the four levels after a change of the external uniaxial stress are then governed by *rate equations*. For the level scheme considered in these experiments (Fig. 1) one obtains

$$\begin{pmatrix} D + \alpha & -p'_{ba} & -2p'_{ca} & -2p'_{da} \\ -p_{ab} & D + \beta & -2p'_{cb} & -2p'_{db} \\ -p_{ac} & -p_{bc} & D + \gamma & -2p'_{dc} \\ -p_{ad} & -p_{bd} & -2p_{cd} & D + \delta \end{pmatrix} \begin{pmatrix} N_a \\ N_b \\ N_c \\ N_d \end{pmatrix} = 0 \quad (2)$$

where

$$D = \partial/\partial t$$

$$\alpha = p_{ab} + 2p_{ac} + 2p_{ad}$$

$$\beta = p'_{ba} + 2p_{bc} + 2p_{bd}$$

$$\gamma = p'_{ca} + p'_{cb} + 2p_{cd}$$

$$\delta = p'_{da} + p'_{db} + 2p'_{dc}$$

$$q = \alpha\beta + \alpha\gamma + \alpha\delta + \beta\gamma + \beta\delta + \gamma\delta$$

$$-p_{ab}p'_{ba} - 2p_{ac}p'_{ca} - 2p_{ad}p'_{da} - 2p_{bc}p'_{cb}$$

$$- 2p_{bd}p'_{db} - 4p_{cd}p'_{dc}$$

$$(3) \quad r = \alpha\beta\gamma + \alpha\beta\delta + \beta\gamma\delta + \gamma\delta\alpha \quad (6)$$

$$-p_{ab}p'_{ba}(\gamma + \delta) - 2p_{ac}p'_{ca}(\beta + \delta) - 2p_{ad}p'_{da}$$

$$\times (\beta + \gamma) - 2p_{bc}p'_{cb}(\alpha + \delta) - 2p_{bd}p'_{db}(\alpha + \gamma)$$

$$- 4p_{cd}p'_{dc}(\alpha + \beta).$$

In these expressions p_{ij} is the probability per unit time for an 'up' rotation from the level i into the higher lying level j . The energy splitting between these two levels can be evaluated for a given stress by means of equations[1]. p'_{ji} is the probability per unit time for the inverse transition. The approach to the Boltzmann distribution in thermal equilibrium requires $p_{ij} = p'_{ji} \exp(-U_{ji}/kT)$. We define the population numbers such that

$$\sum_j g_j N_j(t) = N_0$$

where N_0 is the total number of the molecule and g_j is the degeneracy of the level j . The general solution of the four equations (2) is

$$N_j(t) = \sum_{i=1}^4 c_{ji} \exp(-\lambda_i t) \quad (j = 1, 2, 3, 4) \quad (4)$$

λ_i are the four eigenvalues of the solution. Since the total number of the molecules is constant, one eigenvalue, for instance λ_4 , must be identically zero. The remaining eigenvalues λ_1 , λ_2 and λ_3 correspond to the three relaxation rates $1/\tau_1$, $1/\tau_2$ and $1/\tau_3$ which have been introduced in the preceding chapter. They are the roots of the cubic equation

$$\lambda^3 - p\lambda^2 + q\lambda - r = 0. \quad (5)$$

The coefficients p , q and r are given by

$$p = \alpha + \beta + \gamma + \delta$$

For the evaluation of the 16 coefficients c_{ji} one may choose the 12 independent equations of the system (2) (3 for each of the 4 eigenvalues) and the initial occupation of the 4 levels. Since we start with an unloaded crystal we have $N_j(0) = N_0/6$.

Theoretical expressions for the transition probabilities $p_{ij}(U_{ji}, T)$ have been derived by Gosar and Pirc[4]. It has been shown[1,3] that

cess is. This applies to the present experiments. In this approximation one obtains for the transition probability[4]

$$p_{ij}(U_{ji}, T) = \frac{6\Gamma_\alpha^2 \exp(-2J_\alpha)}{\pi \hbar k^2 T_\alpha^2} \frac{U_{ji}}{\exp(U_{ji}/kT) - 1}. \quad (7)$$

The symbols have the same meaning as in earlier papers[1,3,4]. The index designates the type of the reorientation ($\alpha = 1$ rotation by 90° , $\alpha = 2$ rotation by 60°). Γ_α is the tunneling matrix element for the 'undressed' molecule. The effect of the reorientation of the strain

field is included in a Debye-Waller factor $\exp(-J_a)$. The product $\Gamma_a^* = \Gamma_a \exp(-J_a)$ has been named 'effective' tunneling matrix-element[1].

By means of the equations (1-7) the three relaxation times τ_1 , τ_2 and τ_3 and the sixteen coefficients c_{ij} can be computed for each stress and temperature if the effective tunneling matrix elements Γ_1^* and Γ_2^* are known. Inversely, these two parameters can be determined from the observed time dependences of the populations of the four levels a , b , c and d after change of the external stress. For the following reasons we only used the lowest relaxation rate $1/\tau_3$ to calculate the two parameters Γ_1^* and Γ_2^* :

(1) The two higher relaxation rates $1/\tau_1$ and $1/\tau_2$ could not be separated accurately enough in these experiments.

(2) An evaluation of the 90° tunneling matrix element Γ_1^* using $1/\tau_1$ and $1/\tau_2$ would be very inaccurate, because these two relaxation rates predominantly depend on the rotations by 60° from the levels c and d into the levels a and b .

(3) At low stresses or high temperatures the main contribution to $1/\tau_3$ results from the rotations by 60° , whereas at high stresses or low temperatures the 90° rotations give the main contribution to $1/\tau_3$. Thus, the measurement of $1/\tau_3$ yields both parameters Γ_a^* with about equal accuracy.

(b) Experimental uncertainties

The coefficients p , q and r of equation (5) depend on the temperature T and on the spacing of the four levels a , b , c and d . The temperature was measured with an Allen-Bradley carbon resistor and with the vapour pressure of the helium bath to an accuracy of about 1 per cent. The energy splittings were determined from the equilibrium populations of the four levels. Thus, the effect of friction in the pressure mechanism and deviations from uniaxial stress are to a certain extent automatically taken into account. Nevertheless this procedure is rather inaccurate. Since the

levels a and b are non-degenerate one has to rely on a single EPR line in the determination of the population for each level.

In order to estimate these uncertainties we have also calculated the energy splittings using the generally accepted coefficients b_j and assuming an accurate orientation of the stress axis. The comparison with the measured splittings is summarized in Table 1. We believe that the main source of the discrepancies is the deviation from uniaxial stress.

5. DISCUSSION

(a) Theory and experiment

The two adjustable parameters Γ_1^* and Γ_2^* have been evaluated using only the lowest relaxation rate $1/\tau_3$ (which can be measured accurately) and the experimental energy splittings U_{ba} , U_{ca} and U_{da} . The values of these quantities are listed in the Tables 1 and 2. The Gosar-Pirc theory permits now a complete

Table 1. Comparison of measured and calculated energy splittings of the orientational levels a , b , c and d for the investigated samples. The splittings refer to an uniaxial stress of 10^8 dyn/cm² applied along one of the axes characterized by the angle $\theta = 10^\circ$, 21° or 30°

#	U_{ba} (°K)	U_{ca} (°K)	U_{da} (°K)	
1	0.16	5.9	6.93	$\theta = 10^\circ$
2	0.13	5.13	6.32	
cal	0.15	5.17	6.39	
3	0.69	4.4	6.9	$\theta = 21^\circ$
4	0.75	4.2	7.1	
5	0.57	5.2	7.8	
I	0.74	3.94	6.5	
II	0.90	4.4	7.2	
IV	0.5	4.46	6.5	
V	0.83	4.95	7.5	$\theta = 30^\circ$
cal	0.62	3.97	6.26	
6	1.49	3.06	6.3	$\theta = 30^\circ$
7	1.21	2.66	5.64	
cal	1.21	2.84	5.82	

prediction of the relaxation behaviour of the system. No further adjustable parameters enter. If this theory is really applicable and if

with the experimental observations and support the interpretation outlined in the preceding chapter.

(3) The calculated time dependence of the populations of the four levels agrees with the experiment. As an example we listed in Table 3 the computed coefficients c_{ij} and the relaxation rates $1/\tau_j$ for a given stress and temperature. These values were used to compute the curves shown in Fig. 2.

We did not expect such a good agreement for the following reasons:

(1) The validity of the rate equations for O_2^- in KCl is somewhat in doubt on the basis of the investigations presented in I.

(2) In the Gosar-Pirc theory the reorientation of the molecule is treated on the basis of the adiabatic approximation, which cannot be justified as has been pointed out in I. However the good agreement between their theory and the experimental results suggests that at least in the range of the one phonon processes

Table 2. Effective tunneling matrix elements for the rotation by 60° and 90° . The matrix elements were derived from the measured relaxation rate $1/\tau_3$. Table 2(a) — KCl: $^{16}O_2^-$, Table 2(b) — KCl: $^{18}O_2^-$

#	θ	Γ_1^* (10^{-23} erg)	Γ_2^* (10^{-23} erg)
1	10°	8.1 ± 0.2	—
2	10°	8.1 ± 0.2	—
3	21°	6.5 ± 0.1	26.5 ± 0.2
4	21°	6.8 ± 0.2	24.5 ± 0.4
5	21°	6.9 ± 0.2	23.3 ± 0.4
6	30°	6.2 ± 0.1	24.0 ± 0.2
7	30°	5.9 ± 0.1	24.0 ± 0.2
*	0°	—	28.6 ± 0.2

#	θ	Γ_1^* (10^{-23} erg)	Γ_2^* (10^{-23} erg)
I	21°	2.6 ± 0.1	13.2 ± 0.1
II	21°	3.0 ± 0.2	14.2 ± 0.3
IV	21°	2.4 ± 0.2	11.3 ± 0.3
V	21°	2.5 ± 0.1	13.0 ± 0.3
*	0°	—	18.0 ± 0.1

*These values were obtained from the earlier measurements with the stress along [001].

the rate equations hold, the computed time dependence of the four populations $N_j(t)$ should agree with the experimental results. They do in the following sense:

(1) As illustrated in Figs. 3–5 the calculated relaxation rate $1/\tau_3$ as a function of stress and temperature agrees with the experimental results.

(2) The calculated relaxation rates $1/\tau_1$ and $1/\tau_2$ obey the relation $1/\tau_1 > 1/\tau_2 > 1/\tau_3$; they are of the order of $1/\tau_{001}$ and $1/\tau_{111}$, and show a similar stress and temperature dependence. These results are in qualitative agreement

Table 3. Coefficients c_{ij} and relaxation rates $1/\tau_i$ calculated for $T = 1.52^\circ K$ and $X = 1.92 \cdot 10^8$ dyn/cm² using the two parameters Γ_1^* and Γ_2^* obtained for sample No. 3

N_j/N_0	c_{ij}			
N_a/N_0	—0.165	—0.186	0.185	0.702
N_b/N_0	—0.150	—0.160	0.184	0.292
N_c/N_0	—0.0088	0.172	0.0004	0.0026
N_d/N_0	0.166	0.00034	0.000017	0.0001
$1/\tau_i$ (sec ⁻¹)	0.55	0.345	0.0067	0

corresponding values derived from the earlier measurements with the stress along [001]. The values of these parameters provide a further

test of their interpretation outlined in I and of the theory of Gosar and Pirc[4].

(1) The analysis given in I of the isotope effect in the relaxation rates $1/\tau_{001}$ of $^{18}\text{O}_2^-$ and $^{16}\text{O}_2^-$ indicated that the potential barrier between two equilibrium orientations forming the angle of 60° is not very sensitive to an external stress along [001]. One thus expects that the 60° tunneling rate Γ_2^* derived from the Orbach processes on one hand and from the relaxation rates $1/\tau_{001}$ on the other hand should have roughly the same values. This is in fact observed (compare Table 2). However, the Orbach processes systematically yield somewhat smaller tunneling rates and a 15% larger isotope effect $\Gamma_2^*(^{16}\text{O}_2^-)/\Gamma_2^*(^{18}\text{O}_2^-)$ than do the measurements with the stress along [001]. These results suggest a slightly larger potential barrier for the rotation by 60° than has been reported in I. A slight stress dependence of the barrier which did not show up in the isotope effect $\tau_{001}(^{18}\text{O}_2^-)/\tau_{001}(^{16}\text{O}_2^-)$ might account for this effect. (The previous determination of Γ_2^* was based on measurements of τ_{001} with stresses that were considerably smaller than those required for the present investigation of the Orbach processes).

(2) In I the tunneling rate Γ_1^* could not be derived from the difference of the relaxation rates $1/\tau_{001}$ and $1/\tau_{111}$. The measured ratio τ_{001}/τ_{111} indicated a much smaller tunneling rate for the 90° rotation than for the 60° rotation. This is consistent with the ratio $\Gamma_2^*/\Gamma_1^* \sim 3.5$ (or $p_2/p_1 \sim 10$) derived from the present measurements.

(3) As was shown in I, the isotope effect in the tunneling rates for the two isotopes permits an estimate of an average potential barrier and of an effective moment of inertia of the reorienting defect (molecule plus surrounding strain field). Using the present measurements it is now possible to derive these parameters pertaining to the rotation by 90° which could not be obtained from the earlier measurements with the stress along [001] and [111]. The values of $\Gamma_1^*(^{18}\text{O}_2^-)$ resulting for different samples (Table 2) indi-

cate a slight dependence of the potential barrier upon the angle θ between the stress axis and the [001]-direction. However, the variation of Γ_1^* with the angle θ is so small, that the isotope effect $\Gamma_1^*(^{16}\text{O}_2^-)/\Gamma_1^*(^{18}\text{O}_2^-)$ may be assumed independent of the stress axes used in the present experiments. For the computation of the quantities listed in Table 4 we used

Table 4. Summary of the parameters pertaining to the rotation by 90° calculated from the tunneling matrix elements $\Gamma_1^*(^{18}\text{O}_2^-)$ and $\Gamma_1^*(^{16}\text{O}_2^-)$ which were derived from the measurements with the stress along the axis $\theta = 21^\circ$. The calculation of the effective moments of inertia was based on the model discussed in I. The displacements of the neighbor ions used for this calculation were computed by Muggli[6]*

KCl $\theta = 21^\circ$	90° rotation	
	16	18
$\Gamma_1^*(10^{-24}\text{erg})$	6.73 ± 0.1	2.63 ± 0.1
$\Gamma_1(10^{-23}\text{erg})$	14.1	5.5
Isotope effect	2.57 ± 0.1	
$V_1(10^{-14}\text{erg})$	4.83 ± 0.4	
J_1	3.1	
Γ_1^*/I (exp)	1.41	1.40
Γ_1^*/I (cal)	1.41	1.36

*The equation defining the effective moment of inertia I_e^* given in I should read

$$\frac{I\varphi^2}{2} + \sum_i \frac{M_i r_i^2}{2} = \frac{I_e^* \varphi^2}{2}$$

the isotope effect measured for the stress along $\theta = 21^\circ$. The values listed in this Table are of the same order of magnitude as the corresponding values for the rotation by 60° and they are consistent with the interpretation given in I.

Acknowledgements—We are grateful to Professor W. Känzig for his stimulating interest in this work. We further would like to thank Dr. J. A. Sussmann for a helpful discussion during his visit to Zurich. The experiments described here are a part of a research program supported by the Swiss National Science Foundation.

REFERENCES

1. PFISTER G. and KÄNZIG W., *Phys. condensed Matter* **10**, 231 (1969).
2. ORBACH R., *Proc. R. Soc.* **264**, 458 (1961).
3. SILSBEE R. H., *J. Phys. Chem. Solids* **28**, 2525 (1967).
4. GOSAR P. and PIRC R., *Proc. Int. Conf. Magnetic Resonance, XIV Colloque Ampere, Ljubljana* (1966).
5. KÄNZIG W., *J. Phys. Chem. Solids* **23**, 479 (1962).
6. MUGGLIJ., Thesis.

CATIONIC TRANSPORT IN α -AgI AND α -Ag₂S

C. M. PERROTT*

Department of Physics, University of New England, Armidale N.S.W., Australia

(Received 24 November 1969, in revised form 9 February 1970)

Abstract—The high temperature (α) phases of silver iodide and silver sulphide are known to display marked deviation from the Einstein relation for cationic transport. An interpretation of this effect is suggested in terms of the cation disorder in the materials. It is also shown that, although a critical temperature for cation disordering has been observed in each of these materials by calorimetric investigations, the cationic transport properties are unlikely to be discontinuous at this temperature and the sudden disordering of the structure may not be easily identified by conductivity and diffusion measurements.

1. INTRODUCTION

THERE are marked deviations [1-3] from the Einstein relation for the motion of silver ions in the high temperature (α) phases of silver iodide and silver sulphide and, since the cations seem free to move over a large number of sites within the crystal structures (Fig. 1), the usual theory of correlation effects cannot be applied. Yokota [4] has developed an explanation of these deviations on the basis that, since the activation energies for cationic movement are so very low (~ 0.1 eV) in both materials, a cation on a particular site may be able to jump not only to a vacant neighbouring site but also to an occupied one, thereby inducing the ion on the latter site to jump onwards.

At the time that Yokota published his theory, it appeared that the available cation sites always had equal occupation probability. Recently, however, we identified [5] a rather complex order-disorder transition among the cations in both of these materials. Our calorimetric studies demonstrated that the cation distribution may be described by the following model: the clusters of lattice points near the face and edge centres of the unit cube can only accommodate one cation at a time

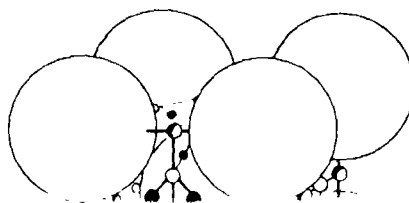


Fig. 1. α -AgI and α -Ag₂S. The large spheres represent anions and the remaining sites, classified according to their symmetry [6-7], are available to the silver ions.

and act as complex sites which define three bcc sublattices in the structure (Fig. 2), the occupancies of which specify the state of order in the cation distribution. If sublattices which are fully occupied at low temperatures are designated σ while those which are then vacant are designated s , the calorimetric data gives their site occupancies as varying in the manner of Fig. 3 and shows that the random distribution ($\sigma = s$) is only achieved at high temperatures (silver iodide has one sublattice of σ type sites and two of s type sites whereas silver sulphide has the reverse).

*Present address: Division of Physics, National Research Council of Canada, Ottawa 7, Canada.

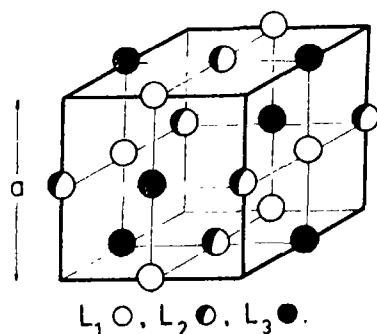


Fig. 2. The three interpenetrating bcc sublattices which specify the configurational distribution of silver ions in α -AgI and α -Ag₂S.

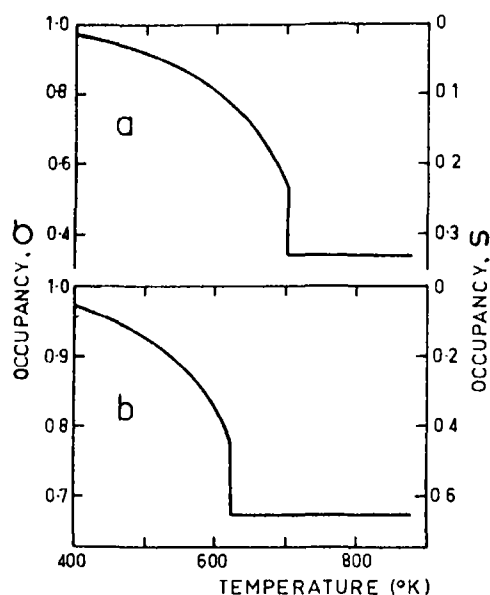


Fig. 3. Variation of the equilibrium values of the order parameters s and σ with absolute temperature in (a) α -AgI, and (b) α -Ag₂S.

Thus, we now have a very different model of the cation distributions in silver iodide and silver sulphide. It is interesting to modify Yokota's theory appropriately, both because experimental data is only available at low temperatures where the differences in the two models are most marked and also because this will provide information about possible

changes in the transport properties near the critical temperature.

2. THEORETICAL DEVELOPMENT

(a) One-dimensional model

Yokota analysed his model in terms of the ionic transport properties of an infinite linear array of equally spaced sites, all of which were taken as having occupation probability p . In order to make this theory applicable to the newer structure model, we need only repeat the analysis for a similar chain in which alternate sites have occupation probability σ and s . Thus, although some points of difference between the two analyses necessarily arise, the basic calculation is unchanged. The first step is to evaluate the self-diffusion coefficient D of a tracer ion by calculating ν , the jump frequency for tracer ion jumps in one direction along the one-dimensional lattice, and using the relationship

$$D = \nu a^2$$

where a is the spacing of lattice sites. Like Yokota, we introduce parameters $\nu_1^{\sigma\sigma}$ and ν_2^{ss} which respectively represent the ion jump frequencies from an occupied site of type s to the neighbouring site of type σ when the latter is vacant and when it is occupied but, in addition, our analysis must include similar parameters for the jumps σ to s and the effect of the overall occupation probability of the site on which the tracer ion is initially supposed to be situated. However, by observing the statistical equilibrium requirement that the total populations of σ and s sites cannot be altered, the second set of parameters can be eliminated and the following expression obtained.

$$\nu = \frac{2s}{s + \sigma} [(\nu_1^{\sigma\sigma} - \nu_2^{ss})(1 - \sigma) + \nu_2^{\sigma\sigma}/(1 - s)],$$

The second step of the calculation is the evaluation of ionic mobility μ . This quantity senses the movement of charge and can be calculated through the effective diffusion coefficient D' for ionic charge (as distinct from tracer ions), thus

$$\mu = \frac{eD'}{kT} = \frac{a^2}{kT} \cdot j$$

where j is the current associated with the numerous ionic jumps accompanying each jump of a tracer ion. Again allowing for the type of the initial tracer position and ensuring that the site occupancies remain invariant, we obtain the result

$$j/e = \frac{2s}{s + \sigma} \left[(\nu_1^{\sigma\sigma} - \nu_2^{ss})(1 - \sigma) + \nu_2^{\sigma\sigma} \left(\frac{1 + \sigma}{1 - \sigma s} \right) \left(\frac{1 + s}{1 - s} \right) \right]$$

which, when combined with our other expressions, shows that ions in this lattice obey a modified form of the Einstein relation, namely

$$\frac{\mu}{D} = f \cdot \frac{e}{kT}$$

The factor f specifies the deviation from the Einstein relation (being unity when no deviation occurs) and has the form

$$f = \{(\nu_1^{ss} - \nu_2^{ss})(1 - \sigma) + \nu_2^{ss} B_1^{ss}\} / \\ [(\nu_1^{ss} - \nu_2^{ss})(1 - \sigma) + \nu_2^{ss} B_2^{ss}]$$

where $B_1^{ss} \equiv (1 + \sigma)(1 + s)/(1 - \sigma s)(1 - s)$ and $B_2^{ss} \equiv 1/(1 - s)$. This simplifies to Yokota's result when $\sigma \approx s \approx p$ and, if σ and s are known, depends on the ratio of jump frequencies as its only parameter. Clearly, deviation from the Einstein relation requires that jumps to occupied sites must be possible (i.e. ν_2^{ss} is not negligible in comparison with ν_1^{ss}).

(b) Application of the model

Although Yokota's result can be applied directly [1] to α -AgI and α -Ag₂S, our expression for the properties of this one-dimensional lattice cannot be applied without careful thought. A high order of approximation requires very complex discussion involving several theoretical parameters which, at present, preclude meaningful comparison with experiment and, since this is our real interest, a zero order treatment using the minimum number of parameters best suits our purpose.

The nature of the cation lattice being considered here is such that ions may only jump directly between 'sites' of different sublattices, each sublattice pair conducting in one axial direction by ionic jumps between nearest neighbour sites and by jumps between next-nearest neighbours in the other two. The crystallographic details ensure that these two types of jump have similar frequencies and it is convenient to adopt an approximate model in which any differences are ignored. Only on such a model, which neglects the probable anisotropy of the crystalline properties, can we proceed directly to a result which is unambiguously applicable to the experimental situation, the available data relating to powdered and fused samples rather than single crystals. On this approximation, any sample has the same properties as a single crystal viewed along a principal axis. Ionic transport along such an axis occurs by jumps which can

involve any pair of sublattices, each jump contributing a step $a/2$ in the field direction. These jumps must occur in such a way that the ionic population of each sublattice remains invariant, a restriction which can best be applied in accordance with Yokota's model by proposing that the positively correlated jumps induced by ionic movement between sites of two sublattices must only involve sites of the same two sublattices. The 'caterpillar mechanism' then involved is identical to that considered above for the one dimensional situation and the results are directly applicable. Each sublattice pair may, however, contribute two parallel links between opposing faces of the unit cube (Fig. 2) and there are three such pairs. Thus, six chains of sites may be active in the transport of cations. Fortunately, these six chains are sufficiently interlaced that any given ion has equal chance of being on any one of them and both the total jump frequency and ionic conductivity are unaffected.

By obtaining the following expression for the deviation from the Einstein relation in α -AgI,

$$f - 1 = \left[\frac{4s}{s + \sigma} (B_1^{ss} - B_2^{ss}) + R(B_1^{ss} - B_2^{ss}) \right] / \\ \left[\frac{4s}{s + \sigma} B_2^{ss} + R B_2^{ss} + A \right].$$

This can be evaluated (with reference to Fig. 3) only if some values can be assigned to the parameters

$$R \equiv \nu_2^{ss}/\nu_2^{ss}$$

$$\text{and } A \equiv \left[\frac{4s}{s + \sigma} (\nu_1^{ss} - \nu_2^{ss})(1 - \sigma) \right]$$

$$\left. + (\nu_1^{ss} - \nu_2^{ss})(1-s) \right] / \nu_2^{ss} \times (1-\sigma) / \nu_2^{ss}.$$

Unfortunately, there is no experimental evidence from which we might separately deduce the detailed behaviour of these quantities and they give the theory great flexibility which can be demonstrated by plotting the theoretical field in which the f factor might fall.

The lower limit to f is always unity, there being no deviation from the Einstein relation when jumps to occupied sites are forbidden ($\nu_2^{ss} = 0$). If the probability of these jumps is allowed to increase, the deviation from the Einstein relation will become greater until the limiting case $\nu_2 = \nu_1$ is achieved (ν_2 cannot exceed ν_1 because it is not physically reasonable that jumps to occupied sites can be more probable than jumps to vacant sites). This limiting situation corresponds to the particular value $A = 0$ but does not imply any restraint on R . This second parameter is necessarily unity at temperatures greater than 700°K, where the distinction between s and σ sites is meaningless, but may be assigned any non-negative value at lower temperatures, zero being the particular value which maximises f . Appropriate substitution in the expression above shows that, for any temperature, the bounds on the deviation from the Einstein relation may be expressed as

$$1 \leq f \leq B_1^{ss}/B_2^{ss},$$

giving the boundary curves 1 and 2 of the field shown in Fig. 4(a).

Silver sulphide has two sublattices of σ type sites and one of s type sites, in which case the theory gives the result

$$f = 1 + \left[\frac{4s}{s+\sigma} r(B_1^{ss} - B_2^{ss}) + (B_1^{ss} - B_2^{ss}) \right] / \left[\frac{4s}{s+\sigma} rB_2^{ss} + B_2^{ss} + a \right]$$

where $r = \nu_2^{ss}/\nu_2^{ss}$

$$\text{and } a = \left[\frac{4s}{s+\sigma} r(\nu_1^{ss} - \nu_2^{ss}) + (\nu_1^{ss} - \nu_2^{ss}) \right]$$

Maximisation of f is achieved by use of the values $r = 0$, $a = 0$ below 623°K (the critical temperature) and $r = 1$, $a = 0$ above that temperature. The limits are

$$1 \leq f \leq B_1^{ss}/B_2^{ss}$$

and are plotted in Fig. 4(b).

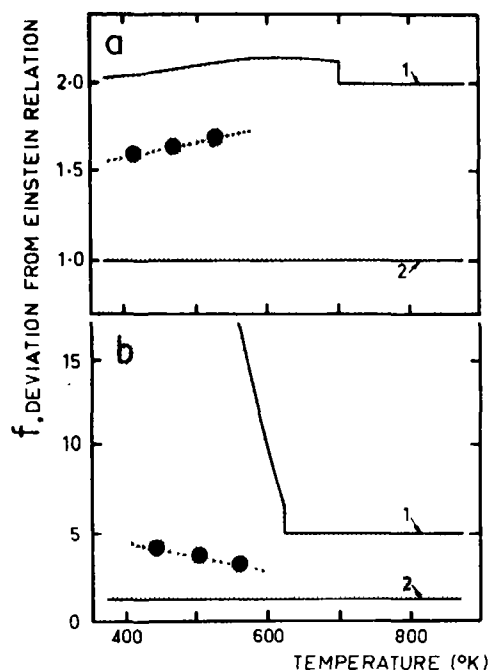


Fig. 4. Experimental values [1] of the f -factor in (a) α -AgI and (b) α -Ag₂S, together with the upper and lower bounds predicted by the present theory

4. DISCUSSION

Our calculations have been based on very similar physical models for α -AgI and α -Ag₂S and, in each case, the experimental values of the quantity f fall within the theoretical field (Fig. 4). There are, however, some factors which might be taken as experimental indication of rather different structural behaviour of the two materials: the deviation

from the Einstein relation in α -Ag₂S is significantly greater and shows a steady decrease with increasing temperature while the reverse is true in α -AgI. Both of these differences are clearly suggested by the width of the theoretical field and its variation with temperature, so we can be confident that these materials are truly very similar, as our calorimetric studies suggested.

Since we have accepted that direct jumps to occupied lattice sites are possible when the average site occupancy is less than unity and we know that such jumps do not occur in fully occupied lattices (where interstitial and vacancy mechanisms apply), should we not expect the ratio ν_1/ν_2 to decrease rapidly as the occupation density decreases? The upper bound shown in Fig. 4 would then represent the limit applicable to very dilute systems and, since the cation densities in α -AgI and α -Ag₂S differ by a factor of two, the experimental results for the two materials should lie at relatively different heights in the plotted fields. This is indeed true, the more dilute α -AgI giving results much nearer to the calculated upper bound.

As far as can be judged from the equation for the critical temperatures (700 and 630°K) the materials will probably not be easily identified from the ionic transport properties although the temperature dependence of the

f factor may be halted as the temperature is increased above the critical value. The present analysis has certainly shown that the available ionic conductivity data, which shows no discontinuity at the critical temperature, is not necessarily at variance with the notion of an order-disorder transition in the materials. However, closer appraisal must await more detailed experimental analysis of the cationic transport processes in these structures, especially at high temperatures.

Acknowledgements—The author is grateful to Professor N. H. Fletcher for interesting discussions on various aspects of this subject and helpful criticism of the manuscript.

This work is part of a program of study of disordered solids financed by the University of New England and the Australian Research Grants Committee and was carried out during the tenure of a postgraduate studentship awarded by the Commonwealth Scientific and Industrial Research Organisation.

REFERENCES

1. OKAZAKI, H. *J. Phys. Chem.*, **71**, 255 (1967).

THE DYNAMIC EFFECTS OF LOCALIZED MAGNETIC MOMENTS ON NUCLEAR SPINS IN METALLIC SYSTEMS*

F. Y. FRADIN

Argonne National Laboratory, Argonne, Ill. 60439, U.S.A.

(Received 6 February 1970)

Abstract—The nuclear spin-lattice relaxation rate of the nonmagnetic species in intermetallic compounds and alloys that possess localized moments is discussed in terms of the generalized dynamic susceptibility of the conduction electrons. The dynamic susceptibility is calculated from an interaction between conduction electrons obtained by Kim, who used a canonical transformation to eliminate (to second order) the s - f (s - d) exchange interaction between conduction electrons and localized spins. The electron interaction obtained leads to a repulsion between electrons of opposite spins in the vicinity of the Fermi surface.

The calculated nuclear spin-lattice relaxation rate has the form

$$1/T_1 = 1/T_{1K} + 1/T_{1f},$$

where $1/T_{1K}$ is the Korringa relaxation rate and $1/T_{1f}$ is the relaxation rate due to the interaction between conduction electrons. The temperature dependence of T_{1f} is discussed for several cases. For intermetallic compounds based on a rare earth or an actinide element combined with a non-transition element, results for both Knight shift and T_1 are consistent with a large density of states at the Fermi level and a small (negative) effective s - f interaction.

1. INTRODUCTION

THE EFFECT of localized magnetic moments on both the static and the dynamic properties of metallic alloys and compounds has been the subject of numerous investigations [1]. A local moment polarizes the conduction electrons via an exchange interaction of the form $-JS \cdot s$, where J is the exchange constant, S is the spin of the local moment, and s is the conduction-electron spin. The conduction-electron polarization is of the form [2] $\cos(2\mathbf{k}_F \cdot \mathbf{r})/(\mathbf{k}_F \cdot \mathbf{r})^3$, where $\mathbf{k}_F$ is the Fermi wave vector. The polarization is coupled to the nuclear spins of the nonmagnetic ions by the contact hyperfine interaction $-AI \cdot s$, where A is the hyperfine constant and I is the nuclear spin. The effect of the static part of the hyperfine interaction is well known. The resonance line of the j th nuclear spin I_j is displaced. In a system in which the local moments reside on

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magnetic ions, the relaxation time T_1 . The relaxation rate $1/T_1$ in simple metals is experimentally found to obey a relation $T_{1K}T = \text{constant}$ over wide temperature ranges. Here T_{1K} is the Korringa [3] value of T_1 , and T is the absolute temperature. The presence of local moments increases $1/T_1$. The local moments in dilute alloys, such as Mn in Cu, result [4] in a temperature-independent contribution to the relaxation rate. The relaxation rate has been discussed by Giovannini and Heeger [5] in terms of a second-order perturbation. Their calculations involve the exchange interaction, the contact hyperfine interaction, and the indirect

*Work performed under the auspices of the U.S. Atomic Energy Commission.

Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction[2] of the form $\mathbf{S} \cdot \mathbf{I}$. They predict a relaxation rate

$$\frac{1}{T_1} = \frac{1}{T_{1k}} \{1 + c\alpha J^2 \ll S_z \gg\},$$

where c is the mole fraction of impurity possessing a local moment, α is a constant, and $\ll S_z \gg$ is the thermal average of the localized spin. When $\ll S_z \gg$ follows the Curie law, the additional term in $1/T_1$ is temperature independent.

The effect of a high concentration of local moments in a chemically ordered system is much more dramatic. We are concerned with T_1 in the paramagnetic state of metallic compounds that order magnetically at low temperature. The local moments give rise to an additional term that dominates $1/T_1$, and that has a complicated temperature dependence. The experimental results have been reviewed recently by Kuznietz *et al.*[6]. A preliminary theoretical discussion has been given by Fradin[7]. The relaxation rate was discussed in terms of the relation

$$\frac{1}{T_1} = \frac{1}{T_{1k}} \{1 + \alpha' |J(\mathbf{Q})|^2 \chi_f(\mathbf{Q})\},$$

where α' is a constant, $J(\mathbf{q})$ is the value of the $\mathbf{q}$ -th Fourier component of the s - f (s - d) exchange interaction, and $\chi_f(\mathbf{q})$ is the wave-vector-dependent susceptibility of the local moment system. $\mathbf{Q}$ is the critical wave vector for magnetic ordering at low temperature[8]. In the molecular field approximation the magnetic energy, neglecting anisotropy, is a minimum at $\mathbf{Q} = 0$ for a ferromagnet and $\mathbf{Q} \neq 0$ for an antiferromagnet.

It is easy to show[8] using the RKKY interaction that the high temperature spin susceptibility can follow a Curie law with *positive* temperature intercept despite the complex magnetic ordering at low temperature. For $J(\mathbf{q})$ independent of $\mathbf{q}$ the paramagnetic Curie temperature is given by $\theta = (J^2/3k_B)[S(S+1)]$

$\chi(\mathbf{q}=0)$, and in the molecular field approximation the ordering temperature is given by $T_{C,N} = (J^2/3k_B)[S(S+1)] \text{Max}_{\mathbf{q}} \chi(\mathbf{q})$. Here $\chi(\mathbf{q})$ is given by

$$\chi(\mathbf{q}) = \frac{1}{N} \sum_{\mathbf{k}, \nu, \mu} \frac{f_{\mathbf{k}+\mathbf{q}, \mu} - f_{\mathbf{k}, \nu}}{\epsilon_{\mathbf{k}+\mathbf{q}, \mu} - \epsilon_{\mathbf{k}, \nu}}$$

where ν and μ are band indices and $f_{\mathbf{k}}$ are the Fermi functions. We define $\text{Max}_{\mathbf{q}} \chi(\mathbf{q}) = \chi(\mathbf{Q})$. The simplest approximation which qualitatively describes the ordering in the rare-earths is the nearly-free electron approximation. Here the Brillouin zone reflections induced by the crystal structure are imposed on the free-electron parabolic bands. For a non-Bravais lattice where $\mathbf{A}$ are vectors of atoms in the unit cell and $\mathbf{G}$ are inverse lattice vectors,

$$\chi^{NFE}(\mathbf{q}) = \sum_{\mathbf{G}} \chi_{\mathbf{q}+\mathbf{G}}^{FE} \phi_{\mathbf{G}}.$$

Here ϕ are the form factors $\phi_{\mathbf{G}} = \sum_{\mathbf{A}} \exp[-i\mathbf{G} \cdot \mathbf{A}]$.

In the present paper we present a general calculation of the relaxation rate based on the effective electron-electron interaction, $\mathcal{H}_e$, mediated by the motion of the localized spins; the interaction has been given by Kim[9]. The flipping motion of the localized spins gives rise to an effective electron-electron interaction that is of the exchange type. It is convenient to express the relaxation rate in terms of the generalized dynamic susceptibility $\chi(\mathbf{q}, \omega)$ of the conduction electrons; this is done in Section 2. In Section 3 $\chi(\mathbf{q}, \omega)$ is calculated from the electron-electron interaction, $\mathcal{H}_e$. The statistical mechanics of the localized moment system is treated in Section 4. Comparison with experimental results is made in Section 5.

2. RESONANCE THEORY

The contact hyperfine interaction between a nuclear spin $\mathbf{I}_i$ and conduction electron spins $\mathbf{s}_j$ may be written

$$\mathcal{H}_1 = -(8\pi/3)\gamma_e\gamma_n\hbar^2\mathbf{I}_i \cdot \sum_j \mathbf{S}_j\delta(\mathbf{r}_{ij}), \quad (2.1)$$

where γ_e and γ_n are the electronic and the nuclear gyromagnetic ratios, respectively, and the $\mathbf{r}_{ij}$ are position vectors between the electrons and the nuclei. The interaction (2.1) gives rise to a shift in the field for nuclear resonance

$$\Delta H = (\gamma_n\hbar)^{-1} \sum_{\mathbf{k}\sigma} A_{\mathbf{k}\mathbf{k}'}\sigma\sigma' m_{\sigma} f_{\mathbf{k}\sigma}, \quad (2.2)$$

where $m_{\sigma} = \pm \frac{1}{2}$ is the spin-projection quantum number and $f_{\mathbf{k}\sigma}$ is the Fermi distribution function for a state with wave vector $\mathbf{k}$ and spin orientation σ . The contact hyperfine coupling parameter $A_{\mathbf{k}\mathbf{k}'}\sigma\sigma'$ is defined in terms of the amplitudes $U_{\mathbf{k}\sigma}(0)$ of the conduction-electron wave functions at the nucleus by

$$A_{\mathbf{k}\mathbf{k}'}\sigma\sigma' = (8\pi/3)\gamma_e\gamma_n\hbar^2 U_{\mathbf{k}\sigma}(0)U_{\mathbf{k}'\sigma'}(0). \quad (2.3)$$

The nuclear spin-lattice relaxation time T_1 of a nonequilibrium system is related to the statistical fluctuations in the equilibrium ensemble by [10]

$$(1/T_1) = (2/\hbar^2) \int_{-\infty}^{+\infty} d\tau \cos(\omega_0\tau) \langle \{\mathcal{H}_I^{\dagger}(\tau)\mathcal{H}_I(0)\} \rangle, \quad (2.4)$$

where ω_0 is the nuclear Larmor frequency and the bracketed term is the symmetric transverse autocorrelation function of the hyperfine interaction equation (2.1).

The natural fluctuations that occur in a system in equilibrium are related by the fluctuation-dissipation theorem [11] to the imaginary part of the linear-response function. The application of the theorem to equation (2.4) yields [10, 12] an expression for the relaxation rate:

$$\frac{1}{T_1} = \frac{2}{\hbar^2} k_B T (\gamma_e\hbar)^{-2} \langle |A_q|^2 \rangle \times \sum_q \omega_0^{-1} \text{Im} \chi'_{-1}(\mathbf{q}, \omega_0), \quad (2.5)$$

where k_B is Boltzmann's constant, T is the ab-

solute temperature, and $\chi'(\mathbf{q}, \omega)$ is the dynamic susceptibility in the direction perpendicular to the field. The usual approximation is made in equation (2.5) that $A_{\mathbf{k}+\mathbf{q},\mathbf{k}} = A_q$ and that it may be averaged separately. Also, we define $H_{\text{eff}}^2 = (\gamma_n\hbar)^{-2} \langle |A_q|^2 \rangle$. The susceptibility function $\chi'(\mathbf{q}, \omega_0)$ has the form of the reduced susceptibility of Izuyama, *et al.* [13] and refers to an electron gas, which differs from a real metal only in that the actual spatial distribution of the electrons is replaced by a uniform distribution. The factorization of a reduced susceptibility from the relevant response function requires that the coupling constants depend only on the wavevector difference between the initial and final states connected by the perturbation.

3. CALCULATION OF THE DYNAMIC SUSCEPTIBILITY

Since our primary interest is to point out a new aspect of nuclear spin-lattice relaxation, we drastically simplify the picture of a metallic solid that possesses localized moments. We

$$\mathcal{H}_I = \sum_{\mathbf{k}\beta} \epsilon_{\mathbf{k}} n_{\mathbf{k}\beta}, \quad (3.1)$$

$$\mathcal{H}_S^z(0) = - \sum_{\mathbf{k}} J(0) a_{\mathbf{k}\beta}^{\dagger} (\sigma_{\beta\beta}^z) a_{\mathbf{k}\beta} S^z(0), \quad (3.2)$$

$$\mathcal{H}_S^{\dagger} = - \sum_{\mathbf{k} \neq 0} J(\mathbf{K}) a_{\mathbf{k}\beta}^{\dagger} \sigma_{\beta\beta'}^{\dagger} a_{\mathbf{k}-\mathbf{K}\beta} \cdot \mathbf{S}(\mathbf{K}), \quad (3.3)$$

where $\mathbf{S}(\mathbf{K}) = N^{-1} \sum_i \exp(-i\mathbf{K} \cdot \mathbf{R}_i) \mathbf{S}_i$, $a_{\mathbf{k}\beta}^{\dagger}$ is the creation operator for a conduction electron with wave vector $\mathbf{k}$ and spin β , $\mathbf{S}_i$ is the localized spin at the atomic site $\mathbf{R}_i$, $J(\mathbf{K})$ is the $\mathbf{K}$ -th Fourier component of the s - f exchange integral, and $n_{\mathbf{k}\beta} = a_{\mathbf{k}\beta}^{\dagger} a_{\mathbf{k}\beta}$. We now use Kim's

canonical transformation[9], which transforms $\mathcal{H}$ to $\mathcal{H}'$; thus, to order J^2 ,

$$\mathcal{H}' = \mathcal{H}_T + \mathcal{H}_{\text{RKKY}} + \mathcal{H}_e + \mathcal{H}_{sf}^z(0). \quad (3.4)$$

Here $\mathcal{H}_{\text{RKKY}}$ is the RKKY interaction, given by

$$\mathcal{H}_{\text{RKKY}} = \sum_{i,j} \mathcal{J}_{ij} \mathbf{S}_i \cdot \mathbf{S}_j. \quad (3.5)$$

$\mathcal{H}_e$ is the effective interaction between conduction electrons given by

$$\begin{aligned} \mathcal{H}_e = -\frac{1}{2} \sum_{\mathbf{l}, \mathbf{l}', \mathbf{K}} C(\mathbf{l}, \mathbf{l}', \mathbf{K}) [& \hbar(a_{\mathbf{l}\uparrow}^\dagger a_{\mathbf{l}-\mathbf{K}\uparrow} \\ & - a_{\mathbf{l}\downarrow}^\dagger a_{\mathbf{l}-\mathbf{K}\downarrow})(a_{\mathbf{l}'\uparrow}^\dagger a_{\mathbf{l}'+\mathbf{K}\uparrow} - a_{\mathbf{l}'\downarrow}^\dagger a_{\mathbf{l}'+\mathbf{K}\downarrow}) \\ & + \frac{1}{2} a_{\mathbf{l}\uparrow}^\dagger (a_{\mathbf{l}-\mathbf{K}\uparrow} a_{\mathbf{l}'\uparrow}^\dagger a_{\mathbf{l}'+\mathbf{K}\downarrow} \\ & + \frac{1}{2} a_{\mathbf{l}\downarrow}^\dagger (a_{\mathbf{l}-\mathbf{K}\downarrow} a_{\mathbf{l}'\downarrow}^\dagger a_{\mathbf{l}'+\mathbf{K}\uparrow})] \end{aligned} \quad (3.6)$$

with

$$\begin{aligned} C(\mathbf{l}, \mathbf{l}', \mathbf{K}) = & -|J(\mathbf{K})|^2 \\ & \times \langle S^z(\mathbf{K}) [(\epsilon_{\mathbf{l}+\mathbf{K}} - \epsilon_{\mathbf{l}} - g\mu_B H^z)^{-1} \\ & - (\epsilon_{\mathbf{l}-\mathbf{K}} - \epsilon_{\mathbf{l}} + g\mu_B H^z)^{-1}] \rangle. \end{aligned} \quad (3.7)$$

Here H^z is the local field at the moment site. The direction of H^z is defined by an infinitesimal external field parallel to the z direction.

We now calculate the dynamic susceptibility of the conduction electrons apart from the form factor, i.e. the reduced susceptibility [13]. The component of the reduced susceptibility that is of interest is the transverse component $\chi'_{\perp}(\mathbf{q}, \omega)$,

$$\begin{aligned} \chi'_{\perp}(\mathbf{q}, \omega) = & g^2 \mu_B^2 \int_{-\infty}^{\infty} e^{-i\omega t} \\ & \times \langle \langle \sigma'_{\perp}(\mathbf{q}, t); \sigma'_{\perp}(-\mathbf{q}) \rangle \rangle dt. \end{aligned} \quad (3.8)$$

Here the spin density operators are given by

$$\sigma'_{\perp}(\mathbf{q}, t) = \sum_{\mathbf{k}} a_{\mathbf{k}+\mathbf{q}\downarrow}^\dagger(t) a_{\mathbf{k}\uparrow}(t) \quad (3.9)$$

and

$$\sigma'_{\perp}(-\mathbf{q}) = \sum_{\mathbf{k}} a_{\mathbf{k}\uparrow}^\dagger a_{\mathbf{k}+\mathbf{q}\downarrow}. \quad (3.10)$$

The conventional definition of the retarded Green's function is used:

$$\langle \langle A(t); B \rangle \rangle = \frac{i}{\hbar} \langle [A(t), B] \rangle \theta(t), \quad (3.11)$$

with

$$\theta(t) = \begin{cases} 1 & t > 0, \\ 0 & t < 0. \end{cases} \quad (3.12)$$

The retarded Green's function may be determined from its equation of motion. Defining $\theta_{\mathbf{k}}(\mathbf{q}, t) \equiv a_{\mathbf{k}+\mathbf{q}\downarrow}^\dagger(t) a_{\mathbf{k}\uparrow}(t)$, we have

$$\begin{aligned} i\hbar \frac{d}{dt} \langle \langle \theta_{\mathbf{k}}(\mathbf{q}, t); \sigma'_{\perp}(-\mathbf{q}) \rangle \rangle = & \\ & -\delta(t) \langle [\theta_{\mathbf{k}}(\mathbf{q}, t), \sigma'_{\perp}(-\mathbf{q})] \rangle \\ & + \langle \langle [\theta_{\mathbf{k}}(\mathbf{q}, t), \mathcal{H}']; \sigma'_{\perp}(-\mathbf{q}) \rangle \rangle. \end{aligned} \quad (3.13)$$

The commutators are given by

$$[\theta_{\mathbf{k}}(\mathbf{q}), \sigma'_{\perp}(-\mathbf{q})] = n_{\mathbf{k}+\mathbf{q}\downarrow} - n_{\mathbf{k}\uparrow}, \quad (3.14)$$

$$[\theta_{\mathbf{k}}(\mathbf{q}), \mathcal{H}_T] = [\epsilon(\mathbf{k}) - \epsilon(\mathbf{k}+\mathbf{q})] \theta_{\mathbf{k}}(\mathbf{q}), \quad (3.15a)$$

$$[\theta_{\mathbf{k}}(\mathbf{q}), \mathcal{H}_{sf}^z(0)] = -2J(0)S^z(0)\theta_{\mathbf{k}}(\mathbf{q}). \quad (3.15b)$$

Within the random phase approximation (RPA)[9, 13]

$$\begin{aligned} [\theta_{\mathbf{k}}(\mathbf{q}), \mathcal{H}_e] \approx & \sum_{\mathbf{K}} C(\mathbf{K}) [\theta_{\mathbf{k}+\mathbf{K}}(\mathbf{q}) \\ & \times (-n_{\mathbf{k}+\mathbf{q}\downarrow} + n_{\mathbf{k}\uparrow}) + \theta_{\mathbf{k}}(\mathbf{q}) \\ & \times (-n_{\mathbf{k}+\mathbf{K}\uparrow} + n_{\mathbf{k}+\mathbf{q}+\mathbf{K}\downarrow})], \end{aligned} \quad (3.16)$$

where we assume from equation (3.7) that only excitation processes near the Fermi surface are important. The Fourier transform of the equation of motion is then

$$\begin{aligned} [-\hbar\omega + \epsilon(\mathbf{k}+\mathbf{q}) - \epsilon(\mathbf{k})] \langle \langle \theta_{\mathbf{k}}(\mathbf{q}, \omega); \sigma'_{\perp}(-\mathbf{q}) \rangle \rangle = & \\ & -(f_{\mathbf{k}+\mathbf{q}\downarrow} - f_{\mathbf{k}\uparrow}) + (f_{\mathbf{k}\uparrow} - f_{\mathbf{k}+\mathbf{q}\downarrow}) \sum_{\mathbf{K}} C(\mathbf{K}) \\ & \times \langle \langle \theta_{\mathbf{k}+\mathbf{K}}(\mathbf{q}, \omega); \sigma'_{\perp}(-\mathbf{q}) \rangle \rangle. \end{aligned} \quad (3.17)$$

Here $\tilde{\epsilon}(k)$ is the one-particle self-energy given by $\tilde{\epsilon}_{\pm}(\mathbf{k}) = \epsilon_{\pm}(\mathbf{k}) \mp J(0)S^z(0) \left(0 + \sum_{\mathbf{K}}' C(\mathbf{K}) f_{\mathbf{k}+\mathbf{K}\pm} \right)$.

Since only excitation processes near the Fermi surface are important, we assume that those terms with $K = Q$ are dominant. Here Q is the critical wave vector spanning the nesting Fermi surface. The dominant term is

$$[-\hbar\omega + \tilde{\epsilon}_\downarrow(\mathbf{k} + \mathbf{q}) - \tilde{\epsilon}_\uparrow(\mathbf{k})]G_{\mathbf{k}+\mathbf{q},\mathbf{k}-\mathbf{q}}^- = [f_{\mathbf{k}\uparrow} - f_{\mathbf{k}+\mathbf{q}\downarrow}] + [f_{\mathbf{k}\downarrow} - f_{\mathbf{k}+\mathbf{q}\uparrow}]C(\mathbf{Q})G_{\mathbf{k}+\mathbf{q},\mathbf{k}-\mathbf{q}}^{++} \quad (3.18)$$

Here G^{++} is the Green's function of equation (3.17). Similarly from equation (3.17) we write the equation for $G_{\mathbf{k}+\mathbf{Q},\mathbf{k}-\mathbf{Q}}^{++}$ as

$$[-\hbar\omega + \tilde{\epsilon}_\downarrow(\mathbf{k} + \mathbf{Q} + \mathbf{q}) - \tilde{\epsilon}_\uparrow(\mathbf{k} + \mathbf{Q})]G_{\mathbf{k}+\mathbf{Q},\mathbf{k}-\mathbf{Q}}^{++} = [f_{\mathbf{k}+\mathbf{Q}\uparrow} - f_{\mathbf{k}+\mathbf{Q}+\mathbf{q}\downarrow}] + [f_{\mathbf{k}+\mathbf{Q}\downarrow} - f_{\mathbf{k}+\mathbf{Q}+\mathbf{q}\uparrow}]C(-\mathbf{Q})G_{\mathbf{k}+\mathbf{Q},\mathbf{k}-\mathbf{Q}}^{++} \quad (3.19)$$

Substituting equation (3.19) into equation (3.18) we find the solution

$$G_{\mathbf{k}+\mathbf{q},\mathbf{k}-\mathbf{q}}^- = \frac{\Gamma_{+\mathbf{k}}(\mathbf{q}, \omega)[1 + C(\mathbf{Q})\Gamma_{+\mathbf{k}+\mathbf{Q}}(\mathbf{q}, \omega)]}{[1 - C(\mathbf{Q})\Gamma_{+\mathbf{k}}(\mathbf{q}, \omega)C(-\mathbf{Q})\Gamma_{+\mathbf{k}+\mathbf{Q}}(\mathbf{q}, \omega)]}$$

valid to all orders in $\tilde{\mathcal{H}}$. Here

$$\Gamma_{\pm\mathbf{k}}(\mathbf{q}, \omega) = \sum_{\mathbf{k}} \Gamma_{\pm\mathbf{k}}(\mathbf{q}, \omega) = \sum_{\mathbf{k}} \frac{f_{\mathbf{k}\uparrow} - f_{\mathbf{k}+\mathbf{q}\downarrow}}{\tilde{\epsilon}_\downarrow(\mathbf{k} + \mathbf{q}) - \tilde{\epsilon}_\uparrow(\mathbf{k}) - \hbar\omega + i\epsilon}$$

In arriving at equation (3.20) we have essentially treated $\chi(\mathbf{q})$ as being proportional to a delta function centered about $\mathbf{q} = \mathbf{Q}$. Though this approach is indeed approximate, it has the virtue of pointing out the physics of the relaxation mechanism, the correlation of an electron of $\mathbf{k}\uparrow$ with a hole of $\mathbf{k} + \mathbf{Q}\downarrow$ at the Fermi level, without relying on detailed band structures.

We have treated a certain class of terms in $\tilde{\mathcal{H}}$ to infinite order in arriving at equation (3.20). However, $\tilde{\mathcal{H}}$ is valid only to second order in the s - f interaction J . The terms that dominate G^{++} and thus the relaxation rate

are those with the small denominator $\epsilon_\downarrow(\mathbf{k} + \mathbf{Q}) - \epsilon_\uparrow(\mathbf{k})$. To estimate the effect of the higher order commutators dropped from $\tilde{\mathcal{H}}$ we may set $\epsilon(\mathbf{I} - \mathbf{K}) - \epsilon(\mathbf{I}) + g\mu_B H_i \approx g\mu_B H_i$ in the denominator of the operator U_i of Ref. [9], since the states $|\epsilon(\mathbf{k} + \mathbf{Q}) - \epsilon(\mathbf{k})| \ll |g\mu_B H_i|$. The higher commutators then lead to renormalization effects of order J/E_F , $(J/E_F)^2$, etc. Thus the truncation of $\tilde{\mathcal{H}}$ to order J^2 is a useful approximation for the relaxation rate problem as long as $N(E_F)J \approx J/E_F \ll 1$. From the calculated quantities in Table 2 $|N(E_F)J| < 10^{-2}$, consistent with the argument.

The denominator in equation (3.20) will henceforth be set equal to unity due to the small effect of the fourth order local moment spin correlation terms in the paramagnetic temperature region. The neglect of this factor is consistent with the neglect of other electron-electron interactions other than $\tilde{\mathcal{H}}$.

The reduced susceptibility, which has the periodicity of the reciprocal lattice, is given by

$$\chi_{\alpha\beta}^{(s)}(\mathbf{q}, \omega) = [1 + C(\mathbf{Q})\Gamma_{+\mathbf{k}+\mathbf{Q}}(\mathbf{q}, \omega)]\chi_{\alpha\beta}(\mathbf{q}, \omega)$$

The superscript (s) indicates the symmetric part of the tensor, i.e. $G_{\alpha\beta}^{(s)} = \frac{1}{2}(G_{\alpha\beta} + G_{\beta\alpha})$.

To calculate the relaxation rate, we substitute equation (3.22) in equation (2.5). The first term in $(1/\omega_0) \sum_{\mathbf{q}} \text{Im} \chi_{\pm\mathbf{q}}^{(s)}(\mathbf{q}, \omega_0)$ is

$$\frac{g^2 \mu_B^2}{2\omega_0} \sum_{\mathbf{q}} \text{Im} \Gamma_{\pm\mathbf{q}}^{(s)}(\mathbf{q}, \omega_0) = \frac{g^2 \mu_B^2}{2} \pi \hbar N(E_F)^2, \quad (3.23)$$

where $N(E_F)$ is the density of states at the Fermi level for *one* spin direction. The combination of equations (3.23) and (2.5) yields

the familiar Korringa[3] term, $1/T_{1K}$, in the relaxation rate:

$$\frac{1}{T_{1K}} = \pi \gamma_n^2 \hbar k_B T H_{hf}^2 N(E_F)^2.$$

The second term in

$$\frac{1}{\omega_0} \sum_q \text{Im} \chi^{(s)}(\mathbf{q}, \omega_0)$$

is given by Σ where

$$\begin{aligned} \Sigma = & \frac{g^2 \mu_B^2}{2\omega_0} \sum_q P \sum_k \frac{f_k - f_{k+q}}{\epsilon(\mathbf{k} + \mathbf{q}) - \epsilon(\mathbf{k}) - \hbar\omega_0} \\ & \times (f_{k+q} - f_{k+q,q}) C(\mathbf{Q}) \\ & \times \delta[\epsilon(\mathbf{k} + \mathbf{Q} + \mathbf{q}) - \epsilon(\mathbf{k} + \mathbf{Q}) - \hbar\omega_0] \\ & + \text{conjugate term} \\ \Sigma = & g^2 \mu_B^2 \pi \hbar \sum_k \left(-\frac{\partial f}{\partial \epsilon_{k+Q}} \right) \\ & \times C(\mathbf{Q}) N(\epsilon_k) \left(-\frac{\partial f}{\partial \epsilon} \right). \end{aligned} \quad (3.24)$$

Because of the delta function properties of the derivatives of the Fermi functions, this equation is essentially a sum over the nested Fermi surface. Thus, from equations (3.23), (3.24) and (2.5) the relaxation rate is given by

$$\frac{1}{T_1} = \frac{1}{T_{1K}} [1 + 2N(E_F)C(\mathbf{Q})]. \quad (3.25)$$

For a dilute random distribution of an impurity with a local moment (as studied by Giovannini and Heeger[5]), we set $C(\mathbf{K}) = C$, independent of $\mathbf{K}$, in equation (3.17). The solution of equation (3.17) is then given by iteration as the sum of an infinite geometric series,

$$\chi^{(s)}_+(\mathbf{q}, \omega) = \frac{\chi^{(s)}_+(\mathbf{q}, \omega)}{1 - cC\chi^{(s)}_+(\mathbf{q}, \omega)} \quad (3.26)$$

where c is the concentration of local moments. If we ignore problems of establishing a nuclear

spin temperature, equation (3.26) leads in general to the type of equations for $1/T_1$ that arise for an electron-electron interaction V that is $\mathbf{q}$ independent[10, 12], except that V is replaced by cC . For $c \ll 1$ we may approximate equation (3.26) by

$$\chi^{(s)}_+(\mathbf{q}, \omega) = \chi^{(s)}_+(\mathbf{q}, \omega) [1 + cC\chi^{(s)}_+(\mathbf{q}, \omega)], \quad (3.27)$$

which leads immediately to

$$\frac{1}{T_1} = \frac{1}{T_{1K}} [1 + 2N(E_F)cC]. \quad (3.28)$$

4. CALCULATION OF $C(\mathbf{K})$

We now calculate $C(\mathbf{K})$ (see equation (3.7)), given by

$$C(\mathbf{K}) = 2|J(\mathbf{K})|^2 \left\langle \frac{S^z(\mathbf{K})}{g\mu_B H^z} \right\rangle. \quad (4.1)$$

Although H^z and S^z are dynamical quantities, they are treated as statistical averages in equation (4.1). Their dynamical nature can be seen from the expression

$$\begin{aligned} \mathcal{H}_{\text{RKKY}} &= \sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j = - \sum_i g\mu_B \mathbf{H}_i \cdot \mathbf{S}_i \\ &= - \sum_i g\mu_B H_i^z S_i^z. \end{aligned} \quad (4.2)$$

Replacement of the operator $\sum_j J_{ij} \mathbf{S}_j$ by its expectation value $-g\mu_B \mathbf{H}_i$ is consistent within the Hartree approximation.

To make clear the meaning of the bracketed quantity in equation (4.1) we calculate the energy E_{loc} in the local field,

$$E_{\text{loc}} = \langle \mathcal{H}_{\text{RKKY}} \rangle = \frac{\text{Tr} e^{-\beta \mathcal{H}} \mathcal{H}_{\text{RKKY}}}{\text{Tr} e^{-\beta \mathcal{H}}} \quad (4.3)$$

with $\beta = 1/k_B T$ and $\mathcal{H}$ the total Hamiltonian of the localized electron system.

In the high-temperature approximation

$$E_{\text{loc}} = \frac{-\beta \text{Tr} \mathcal{H}_{\text{RKKY}}^2}{\text{Tr} 1} = - \sum_{ij} J_{ij}^2 \frac{[S(S+1)]^2}{3k_B T}.$$

Since the system is assumed to be translationally invariant, we have

$$E_{\text{loc}} = -N \sum_j \mathcal{J}_{ij}^2 [S(S+1)]^2 / 3k_B T.$$

We define the square of the local field by

$$H^2 = \sum_i \mathcal{J}_{ij}^2 S(S+1) / g^2 \mu_B^2,$$

and we find

$$\begin{aligned} \langle S^z / g \mu_B H^z \rangle &= \langle -E_{\text{loc}} / N g^2 \mu_B^2 H^2 \rangle \\ &= \frac{S(S+1)}{3k_B T}. \end{aligned} \quad (4.5)$$

Thus $C(\mathbf{K})$ depends on the statistical average of the spin in its local field.

We can rewrite equation (4.2) as

$$\mathcal{H}_{\text{RKV}} = \sum_{\mathbf{q}} \mathcal{J}(\mathbf{q}) \mathbf{S}(-\mathbf{q}) \cdot \mathbf{S}(\mathbf{q}). \quad (4.6)$$

Thus equation (4.1) may be calculated self-consistently as

$$C(\mathbf{K}) = 2 |J(\mathbf{K})|^2 G^{zz}(\mathbf{K}, 0).$$

Here the spectral density $G^{\alpha\beta}(\mathbf{q}, \omega)$ is in the molecular-field approximation by

$$\begin{aligned} \langle S_i^\alpha(t) S_j^\beta(t') \rangle &= \int d\omega e^{i\omega(t-t')} \sum_{\mathbf{q}} e^{i\mathbf{q} \cdot (\mathbf{R}_i - \mathbf{R}_j)} \\ &\times G^{\alpha\beta}(\mathbf{q}, \omega), \end{aligned} \quad (4.8)$$

with

$$G^{\alpha\beta}(\mathbf{K}, \omega) = \frac{G_0^{\alpha\beta}(\omega)}{1 + \lambda(\mathbf{K}) G_0^{\alpha\beta}(\omega)} \quad (4.9)$$

and

$$G_0^{zz}(\omega) = 2 \sum_{\nu, \nu'} \frac{\langle \nu | S^z | \nu' \rangle \langle \nu' | S^z | \nu \rangle \sinh \left[\frac{\beta(\epsilon_\nu - \epsilon_{\nu'})}{2} \right]}{\left[\cosh \left(\frac{\beta \epsilon_\nu}{2} \right) \cosh \left(\frac{\beta \epsilon_{\nu'}}{2} \right) \right] [\hbar \omega + \epsilon_\nu - \epsilon_{\nu'}]}, \quad (4.10)$$

where $\lambda(\mathbf{K})$ is the wave-vector-dependent constant of the molecular field.

Consider eigenstates of the individual local moment spin $|\nu\rangle = |S m_s\rangle$; then

$$\begin{aligned} G_0^{zz}(0) &= 2 \sum_{m, m'} \frac{|\langle m_s | S^z | m_s \rangle|^2 \sinh \left[\beta \frac{E_m - E_{m'}}{2} \right]}{\cosh \left(\beta \frac{E_m}{2} \right) \cosh \left(\beta \frac{E_{m'}}{2} \right) [E_m - E_{m'}]} \\ &= 2 \sum_m \frac{|\langle m_s | S^z | m_s \rangle|^2}{\cosh^2 \beta \frac{E_m}{2}} \frac{\beta \lim_{\beta \rightarrow 0} \frac{\sinh(\beta \chi/2)}{\beta \chi/2}}{2}. \end{aligned} \quad (4.11)$$

For $\beta(E_m/2) \ll 1$, we use the high-temperature approximation to find

$$G_0^{zz}(0) = \beta \text{Tr}(S^z)^2 = \beta S(S+1) \quad (4.12)$$

in agreement with equation (4.5). Thus, from equation (4.9)

$$\frac{1}{T_1} = \frac{1}{T_{1K}} \left[1 + \frac{4N(E_f)S(S+1)|J(\mathbf{Q})|^2}{3k_B[T - \theta(\mathbf{Q})]} \right], \quad (4.14)$$

where

$$\theta(\mathbf{Q}) = -\lambda(\mathbf{Q}) \frac{S(S+1)}{3k_B}. \quad (4.15)$$

For the impurity (see equation (3.28)), $\theta(\mathbf{K}) \equiv 0$; if we replace $|J(\mathbf{Q})|^2$ by J^2 , the relaxation rate becomes

$$\frac{1}{T_1} = \frac{1}{T_{1K}} \left[1 + \frac{4N(E_f)cS(S+1)J^2}{3k_B T} \right]. \quad (4.16)$$

(4.10) with $c \ll 1$.

Consider eigenstates of the total angular momentum, j , $|\nu\rangle = |jM_j\rangle$. If j mixing can be ignored, we can employ the operator equivalent $S_z = (g_j - 1)j_z$. Then equation (3.25) becomes

$$\frac{1}{T_1} = \frac{1}{T_{1A}} \left[1 + 4N(E_F)(g_j - 1)^2 \times \frac{j(j+1)|J(\mathbf{Q})|^2}{3k_B(T - \theta(\mathbf{Q}))} \right]. \quad (4.17)$$

5. COMPARISON WITH EXPERIMENT

In this section we compare our theoretical results with the experimental results for $1/T_1$ for the nucleus of one of the nonmagnetic ions in intermetallic compounds in which one of the other chemical species has a local moment. We will ignore j mixing and crystal-field effects [17] in order to simplify the comparison. Thus, the appropriate theoretical relation for the relaxation rate is that given by equation (4.17). We also make use of the relation between the Knight shift K and the susceptibility. The relation is found by use of equations (2.2) and (3.13)–(3.15), with the assumption that the susceptibility is isotropic:

$$K = (H_{hf}/\mu_B) R c \chi'_{zz}(0, 0) = 2\mu_B H_{hf} N(E_F) \times \left[1 + \frac{J(0)\langle S^2(0) \rangle}{2\mu_B H} \right], \quad (5.1)$$

$$K = K_0 + JN(E_F)H_{hf}(g_j - 1)\chi_f/Ng_j\mu_B. \quad (5.2)$$

In equation (5.2) $K_0 = 2\mu_B H_{hf} N(E_F)$ and $(g_j - 1)\chi_f H = Ng_j\mu_B \langle S^2(0) \rangle$, where K_0 is a temperature-independent term and J is the uniform term in the Fourier decomposition of the s - f interaction.

To include structure factors, which were neglected in equations (2.2) and (2.5), equations such as (4.17) and (5.1) must be modified as follows: Multiply the second term by $\cos \mathbf{G} \cdot \mathbf{r}$, replace $\mathbf{q}$ by $\mathbf{q} + \mathbf{G}$, and sum over $\mathbf{G}$. Here $\mathbf{G}$ is a reciprocal lattice vector and $\mathbf{r}$ is the position of the nucleus in the unit cell. For simplicity, in what follows, we consider only

$\mathbf{G} = 0$. Using the eigenvalues $|\nu\rangle = (jM_j)$ [as in the derivation of equation (4.17)], we have from equation (5.2)

$$K = K_0 + [JN(E_F)H_{hf}(g_j - 1)g_j \times \frac{\mu_B j(j+1)}{3k_B(T - \theta)}]. \quad (5.3)$$

Since K_0 and $(T_{1K}T)^{-1}$ are small and temperature independent, the quantities

$$\lambda = JN(E_F)H_{hf}(g_j - 1)g_j\mu_B j(j+1)/3k_B \quad (5.4)$$

and

$$\eta = 4\pi\gamma_n^2 \hbar k_B H_{hf}^2 N(E_F)^3 J^2(\mathbf{Q}) \times (g_j - 1)^2 j(j+1)/3k_B \quad (5.5)$$

can be determined from the reciprocal slopes of the plots of $(K - K_0)^{-1} \equiv K_f^{-1}$ vs. T and of $[(T_1 T)^{-1} - (T_{1K} T)^{-1}]^{-1} \equiv (T_{1f} T)$ vs. T , respectively. Once η and λ are known, we can determine $N(E_F)$ from

$$\eta = 4\pi\gamma_n^2 \hbar k_B N(E_F) \frac{3k_B}{g_j^2 \mu_B^2 j(j+1)} \lambda^2. \quad (5.6)$$

In equation (5.6) we have assumed for simplicity that $J(\mathbf{Q}) = J$.

We now focus attention on the intermetallic compounds PuP, UP_{1-x}S_x, PrAl₂ and NdAl₂, for which data exist on the spin-lattice relaxation of the nucleus of the nonmagnetic species [6, 17, 18] (either ³¹P or ²⁷Al). The data for the temperature range $T_{c,n} < T < 3T_{c,n}$, where $T_{c,n}$ is either the Curie or Néel temperature, are of interest. In this temperature range the relaxation rate $1/T_1$ is dominated by the second term, $1/T_{1f}$, in equation (4.17).

For these compounds, the susceptibility follows a Curie-Weiss-like behavior over the temperature range of interest. Thus, with the definitions $\alpha \equiv dK/d\chi_f$ and $p^2 \equiv g_j^2 j(j+1)$, we can write equation (5.6) as

$$\eta = 4\pi\gamma_n^2 \hbar N(E_F) \frac{N^2 \mu_B^2 p^2}{3} \alpha^2. \quad (5.7)$$

For ^{31}P equation (5.7) gives

$$\eta = 10.1 [N(E_F) \text{ eV}^{-1}] p^2 \alpha^2,$$

and for ^{27}Al

$$\eta = 4.18 [N(E_F) \text{ eV}^{-1}] p^2 \alpha^2.$$

The relaxation rate in the compounds is found to be independent of magnetic field for fields of the order of 10 G. Table 1 lists the relevant magnetic and nuclear magnetic resonance parameters found by experiment. Note that a rough correspondence exists between $\theta(\mathbf{Q})$ (the temperature at which $T_{1f}T$ crosses the T axis) and the ordering temperature for compounds that exhibit either antiferromagnetic or ferromagnetic order at low temperatures. However, there is no correspondence between the Curie-Weiss temperature, θ , and $\theta(\mathbf{Q})$ in those compounds that order antiferromagnetically at low temperature. The behavior of $\theta(\mathbf{Q})$ is indicative of the fact that above the ordering temperature the spin-lattice relaxation rate is influenced by the wavevector-dependent correlations of short-range magnetic order. These correlations are significant at temperatures of less than twice the ordering temperature. Since the indirect coupling between localized mo-

has a peak for $\mathbf{q} = \mathbf{Q} \neq 0$ for antiferromagnets [8], we expect $\theta = \theta(\mathbf{q} = 0)$ to be less than $\theta(\mathbf{Q})$. The ordering temperature, however, is determined by the first fluctuation that becomes critical, and therefore correlates with $\theta(\mathbf{Q})$.

Because of the simple model used to describe the conduction electrons and the simple form of the conduction electron-nuclear spin interaction, we cannot place too much significance on the quantitative values of $N(E_F)$, or of the s - f coupling constant J that are derived from equations (5.7) and (5.3). Effects due to the band structures, electron-electron interactions mediated by either Coulomb or paramagnon interactions, and the core-polarization interaction with the nucleus due to the d -like conduction electrons are probably quite important.

The calculations are highly model-dependent both as to the treatment of the conduction electrons and of the electron-nuclear interaction. The view of the localized moments is also over-simplified. However, we may determine

Table 1. Magnetic and nuclear

	PuP ^a	UP ^b	UPu _{0.8} Sn _{0.2} ^b	UPu _{0.7} Sn _{0.3} ^b	UPu _{0.5} Sn _{0.5} ^b	PtAl ^c	NiAl ^c
Type of order	<i>F</i>	<i>AF</i>	<i>AF</i>	<i>F</i>	<i>F</i>	<i>F</i>	<i>F</i>
Ordering temperature (°K)	126	125	102	102	150	34	65
Paramagnetic moment (μ_B)	1.0	3.19	3.10	2.83	2.75	3.5	3.1
θ (°K)	135	32	73	102	146	32	61
$\theta(\mathbf{Q})$ (°K)	137 ± 15	140 ± 8	124 ± 18	130 ± 20	141 ± 15	38	55
$\alpha = dK/d\chi_f$ (c.m.u./mole) ^d	16.7 ± 0.2	4.0 ± 0.5	4.0 ± 0.5	4.0 ± 0.5	4.0 ± 0.5	0.94	1.1
$\eta^{-1} = d(T_{1f}T)/dT$ (m sec)	0.23	0.63	0.53	0.61	0.66	6.9	4.2

^aRefs. [7], [17].

^bRefs. [6], [19], [20].

^cRefs. [1], [18], [21].

^dRefs. [1], [18], [22].

Table 2. Derived values of the density of states and the exchange coupling

	PuP	UP _{1-x} S _x ^a	PrAl ₂	NdAl ₂
$N(E_F)$ (states/eV-atom)	1.5	1.2	3.2	4.9
H_{hf} (10 ⁶ G)	7.6	7.6	6.6	6.6
J (eV)	-4×10^{-3}	-8×10^{-3}	-1×10^{-3}	-5×10^{-4}
J_K (eV) ^b	-0.98	-2.4	-0.48	-0.38

^aValues of $p = 2.67$, $\alpha = 4.0$ mole/e m.u., and $\eta^{-1} = 0.60 \times 10^{-1}$ sec are used to describe the average behavior of the four UP_{1-x}S_x compounds.

^bCalculated from equations (5.1) and (5.2) using the Knight shifts in the nonmagnetic isostructural compounds to estimate the produces $N(E_F)H_{hf}$.

$N(E_F)$, the values of H_{hf} estimated from Goudsmit's relation, and Russel-Saunders values of g_J for 3+ ions. The values of J , designated J_K , calculated from the Knight shift [1] alone are also shown in Table 2. The values of $N(E_F)$ and J in Table 2 should be taken as order of magnitude estimates.

The method used for the calculation of J_K essentially assumes a small free electron density of states. The elimination of the unknown quantities by combining the data for the Knight shift and for T_1 yields values of $N(E_F)$ and J that have better correspondence with experimental and theoretical knowledge of the 4f and 5f metals. That is, the large $N(E_F)$ is consistent with the large electronic specific heat found in d-electron metals [23]. The small J values are consistent with the competition between exchange ($J > 0$) and small interband mixing ($J < 0$) [24] predicted theoretically [25], and with the g factors measured by electron spin resonance [26] on rare earth systems.

Since a rather drastic assumption about the q dependence of the conduction-electron susceptibility $\chi(q)$ was employed in equation (3.25) the linearity of (T_1/T) vs. T is not *a priori* certain. In fact, deviations from linearity in compositions [6] of UP_{1-x}S_x other than those discussed here do exist, and a more complete treatment is necessary to handle this problem. The calculation requires a knowledge of the details of the band structure or, more specifically, of $\chi(q)$. Finally, the

treatment of the statistical mechanics of the local moments in Section 4 is not appropriate when strong interband mixing couples the local moments to the conduction electrons as occurs in the Kondo problem for $T < T_{\text{Kondo}}$.

Acknowledgements—The author would like to thank Dr. S. Chan and Dr. A. J. Freeman for critically reading the manuscript. Dr. M. Kuznietz kindly made his data on the UP-US system available prior to publication.

REFERENCES

1. A compilation of resonance results in rare-earth intermetallic compounds can be found in JONES F. D., *Phys. Rev.* **180**, 455 (1969).
2. Yosida K., *Phys. Rev.* **106**, 893 (1957).
3. KORRINGA J., *Physica* **16**, 601 (1950).
4. LUMPKIN O. J., *Phys. Rev.* **164**, 324 (1967).
5. LEVINE R. E., *Phys. Lett.* **28A**, 504 (1969).
6. GIOVANNINI B. and HEEGER A. J., *Solid State Commun.* **7**, 287 (1969).
7. KUZNIETZ M., BASKIN Y. and MATZKANIN G. A., *Phys. Rev.* **187**, 737 (1969).
8. FRADIN F. Y., *Solid State Commun.* **7**, 759 (1969).
9. DONIACH S., in Italian Physical Society, *Proceedings of the International School of Physics* (Edited by W. Marshall) Vol. 37, p. 255. Academic Press, New York (1967); EVENSON W. E. and LIU S. H., *Phys. Rev. Lett.* **21**, 432 (1968).
10. KIM D. J., *Phys. Rev.* **149**, 434 (1966); KIM D. J., *Phys. Rev.* **167**, 545 (1968).
11. MORIYA T., *J. phys. Soc. Japan* **18**, 516 (1963).
12. KUBO R. and TOMITA K., *J. phys. Soc. Japan* **9**, 888 (1954); KUBO R., *J. phys. Soc. Jap.* **12**, 570 (1957).
13. NARATH A. and WEAVER H. T., *Phys. Rev.* **175**, 373 (1968).
14. IZUYAMA T., KIM D. J. and KUBO R., *J. phys. Soc. Japan* **18**, 1025 (1963).
15. KADANOFF L. P., *Phys. Rev.* **132**, 2073 (1963).
16. DONIACH S., *J. appl. Phys.* **39**, 483 (1968).
17. CHAN S., (To be published).

17. LAM D. J., FRADIN F. Y. and KRUGER C. I., *Phys. Rev.* **187**, 606 (1969).
18. SILBERNAGEL B. G., JACCARINO V., PINCUS P. and WERNICK J. H., *Phys. Rev. Lett.* **20**, 1091 (1968).
19. ALLBUTT M. and JUNKISON A. R., *AERE-HARWELL, UK, CHEM. Div. Rep. No. AERE-R5465* (1967).
20. KUZNIETZ M., LANDER G. H. and BASKIN Y., *J. appl. Phys.* **40**, 1130 (1969).
21. NERESON N., OLSEN C. and ARNOLD G., *J. appl. Phys.* **39**, 4605 (1968).
22. NERESON N., OLSEN C. and ARNOLD G., *J. appl. Phys.* **37**, 4575 (1966).
23. LOUNASMAA O. V., *Phys. Rev.* **133**, A211 (1964).
- deCOMBARIEN A., COSTA P. and MICHEL J., *Compt. Rend.* **5521**, (1963). COUNSFILL J. F., DELL R. M., JUNKISON A. R. and MARTIN J. F., *Trans Faraday Soc.* **63**, 72 (1967).
24. SCHRIEFFER J. R. and WOLFF P. A., *Phys. Rev.* **149**, 491 (1966); ANDERSON P. W., *Phys. Rev.* **124**, 41 (1961).
25. WATSON R. E., KOIDE S., PETER M. and FREEMAN A. J., *Phys. Rev.* **139**, A167 (1965).
26. JACCARINO V., MAITHIAS B. T., PETER M., SUHL H. and WERNICK J. H., *Phys. Rev. Lett.* **5**, 251 (1960), SHALTIEL D., *Hyperfine Interactions* (Edited by A. J. Freeman and R. B. Frankel), Academic Press, New York (1967).

MÖSSBAUER STUDIES OF THE CHARGE TRANSFER PROCESS IN THE SYSTEM $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$

D. C. DOBSON, J. W. LINNETT and M. M. RAHMAN

Department of Physical Chemistry, University of Cambridge, England

(Received 6 February 1970)

Abstract—The ferrite system $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$ was investigated by taking Mössbauer spectra and measuring electrical resistivities of samples with several values of x . For $x \leq 0.6$, each sample showed two Zeeman patterns in the Mössbauer spectra which are attributed to tetrahedral and octahedral cations respectively. The spectrum due to octahedral cations appeared to be composite and an explanation is given. When $x \geq 0.8$, the spectra showed only quadrupole splitting. From these observations, it appears that fast electron hopping occurs among octahedral sites for $x \leq 0.6$. This conclusion, together with the variation of conductivity with x , suggests that the system is metallic in type in the range $0 \leq x \leq 0.6$, and n -type semiconducting in the range $0.8 \leq x \leq 1.0$.

1. INTRODUCTION

THE ELECTRICAL and magnetic properties of magnetite and related ferrites are of academic and technical interest. In spite of a great deal of work as reviewed recently [1-4], the charge transfer processes in these materials, as well as other transition metal oxides, are still not well understood.

Magnetite, Fe_3O_4 , has an inverse structure [5]. The unit cell has the formula $(\text{Fe}^{3+})_t[\text{Fe}^{3+}\text{Fe}^{2+}]_o\text{O}_{32}$ where the scripts t and o refer to tetrahedral and octahedral sites respectively in the fcc lattice of the O^{2-} ions. Although all the superexchange interactions between cations in magnetite are negative, the interaction between the sub-lattices is the dominant one, and as a result the spins of cations are ordered parallel within individual sub-lattices, but the two sub-lattice spins are anti-parallel to each other [6]. This makes magnetite a ferrimagnet. If the tetrahedral ferric ions are progressively replaced by diamagnetic Zn^{2+} ions (Zn^{2+} is known to prefer tetrahedral sites in ferrites [7]), materials with the formula $(\text{Zn}_x\text{Fe}_{1-x}^{3+})_t[\text{Fe}_{1-x}^{3+}\text{Fe}_{1-x}^{2+}]_o\text{O}_4$ are obtained. The spinel lattice is retained throughout the range $0 \leq x \leq 1$. With $x = 1$, we obtain the normal spinel $(\text{Zn})_t[\text{Fe}_2]_o\text{O}_4$, which is antiferromagnetic (Neel temperature

9.5°K) as the intersub-lattice exchange interaction is absent.

In magnetite, there are equal numbers of ferrous and ferric ions in the octahedral sites. There is an exchange of electrons between neighbouring cations, and this is believed to be

This study was undertaken to illuminate some aspects of electron movement in the system. Electrical resistivity measurements have also been performed to supplement the results

2. EXPERIMENTAL

(a) Preparation of samples

Appropriate proportions of 'specpure' ferric oxide, analar grade zinc oxide and iron powder were mixed thoroughly in a mortar and the resulting mixture heated in evacuated sealed tubes at 950°C for seven hours. The products were cooled slowly. X-ray powder photographs of the samples were taken with a

Gunnier camera and the diffraction pattern showed the presence of a single spinel phase. The samples were analysed for iron and zinc content by X-ray fluorescence. The ferrous iron content was determined by dissolving a weighed quantity of the sample in hydrochloric acid in an atmosphere of carbon dioxide, and then titrating against standard potassium dichromate solution. The results of analysis are shown in Table 1. Samples prepared in this way were used only for Mössbauer studies.

(b) Mössbauer experiments

Spectra were obtained using a 5 mc ^{57}Co source (diffused into 6μ Pd) mounted on a vibrator (Pye-Ling) operated in a linear velocity mode. Detection was by a NaI (TI) scintillator-photomultiplier (EMI 9536A) combination followed by pulse height analysis. Data was stored in a 1600 word memory unit (RIDL 22-01) with punched tape output and an oscilloscope display. Data analysis was carried out on the Titan Computer in the University of Cambridge Mathematical Laboratory.

Soft iron, stainless steel and sodium nitroprusside standard absorbers were used to calibrate the velocity scale. Powder samples were fabricated into discs, using a metallurgical mounting plastic (North Hill Plastics Ltd) with an iron density of approximately 10 mg/cm². Isomer shifts were measured with respect to the standard sodium nitroprusside

spectrum. All spectra were recorded at room temperature.

(c) Resistivity measurements

Mixtures containing appropriate proportions of the starting materials were compressed under a pressure of 8 tons/in² and pellets of 1.22 cm dia. and thickness of the order of a few mm were obtained. These pellets were fired to a temperature of 950°C in a closed evacuated system for 7 hr. The faces of the pellets were polished using emery paper. For resistivity measurements, a pellet was placed between two electrodes of thick copper foils pressed between two perspex sheets by screws. The assembly was placed in an enclosed glass system, the leads being taken out through ceramic seals. The resistivity was measured by a Wayne Kerr Autobalance Universal Bridge (Model B641). The assembly was evacuated before making any measurements.

After the resistivity measurements, the pellets were crushed and were analysed for their total and ferrous iron content, zinc content, by the methods mentioned in (a). The results of analysis are included in Table 1.

3. RESULTS

Figure 1 shows the Mössbauer spectra of samples with $x = 0.0, 0.2, 0.4$ and 0.6 . The sample with $x = 0$ (i.e. Fe_3O_4) gave the expected spectra consisting of two Zeeman patterns *a* and *b* as indicated in the figure. The

Table 1. Results of analysis of the samples of $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$

Value of x				Atomic ratios				
Nominal	Analysed*			Total Fe/Zn			Fe ²⁺ /Zn	
	Powder	Pellet	Calc.	Powder	Pellet	Calc.	Powder	Pellet
0.0	0.0	0.0	∞	—	—	∞	—	—
0.2	0.23	0.17	14.0	13.0	16.1	4.0	3.7	4.9
0.4	0.40	0.34	6.5	6.3	7.8	1.5	1.6	2.0
0.6	0.57	0.50	4.0	4.1	5.5	0.67	0.75	1.2
0.8	0.76	0.73	2.8	2.8	3.4	0.25	0.31	0.38
1.0	0.99	0.86	2.0	2.0	2.2	0.00	0.01	0.17

* The analysed value of x has been obtained from the experimental ratio Fe^{2+}/Zn .

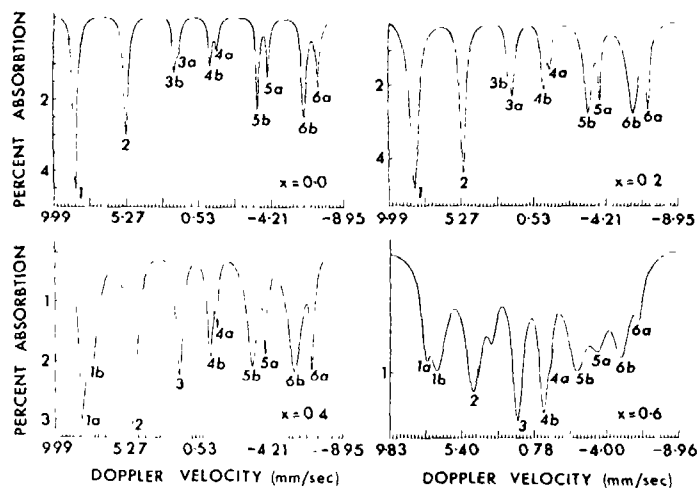


Fig. 1. Mössbauer spectra of samples belonging to the system $\text{Zn}_{1-x}\text{Fe}_x\text{O}_4$. The nominal values of x are indicated. The magnetic hyperfine patterns are indicated by numbering the lines from 1 to 6, and appropriate subscripts for the resolved lines. For $x = 0.6$, the lines marked 3 and 4b are considered to be the quadrupole split pattern c .

pattern a is due to tetrahedral ferric ions and b is due to octahedral ferrous and ferric ions rendered indistinguishable by electron hopping at a frequency faster than that of Larmor precession of the iron nucleus hyperfine field. The percentages of the area represented by each pattern have been calculated by considering the 6th lines, since these are the best resolved. The percentages agree quite well with the percentages of the total number of iron atoms on each site. This confirms the fact, demonstrated previously[11], that the areas of Lorentzian lines for powder samples of similar thickness are proportional to the concentration of absorbing species.

The spectra of samples with $x = 0.2$ and 0.4 consisted of fairly sharp and Lorentzian lines, which are best explained by two overlapping Zeeman patterns a and b , similar to those of Fe_3O_4 . The lines unique to a are sharp, but those unique to b are broader so that the pattern b appears to be composite. An unambiguous deconvolution of the lines was not possible; nevertheless, it appears that the

pattern b might be the resultant of several overlapping Zeeman patterns. The spectrum of the sample with $x = 0.6$ has rather broad

Fe_3O_4 . For the sample with $x = 0.6$, the contribution of the quadrupole split spectrum c was estimated by comparison with the spectrum of the sample with $x = 1$.

The spectrum of the sample with $x = 0.7$ showed several Gaussian lines, indicating some magnetic ordering in the sample. But no systematic analysis was possible. The spectra of samples with $x = 0.8$ and 1 showed only quadrupole splittings. Mössbauer parameters calculated from the above spectra are summarised in Table 2.

The variation of the resistivities with composition for the samples at room temperature

Table 2. Collected results from Mössbauer spectra

Value of x nominal	Pattern	Isomer shift (mm/sec)	Quadrupole splitting $1/2e^2qQ$ (mm/sec)	H_{eff} (kOe)	A_a	A_c
0.0	<i>a</i>	0.56 ± 0.05	-0.04 ± 0.05	495 ± 5	34	33.4
	<i>b</i>	0.95 ± 0.05	$+0.06 \pm 0.05$	458 ± 5	66	66.6
0.2	<i>a</i>	0.51 ± 0.05	-0.04 ± 0.05	483 ± 5	25	27.8
	<i>b</i>	0.94 ± 0.05	$+0.10 \pm 0.05$	447 ± 5	75	72.2
0.4	<i>a</i>	0.51 ± 0.05	$+0.04 \pm 0.05$	472 ± 5	19	23.2
	<i>b</i>	0.87 ± 0.05	-0.14 ± 0.05	412 ± 10	81	76.8
0.6	<i>a</i>	0.55 ± 0.10	$+0.10 \pm 0.10$	437 ± 20	15	17.8
	<i>b</i>	1.03 ± 0.10	-0.38 ± 0.10	353 ± 30	70	76.8
	<i>c</i>	0.61 ± 0.10	(1.70 ± 0.10)	—	15	
0.8	<i>c</i>	0.78 ± 0.05	0.32 ± 0.05			
1.0	<i>c</i>	0.69 ± 0.03	0.33 ± 0.03			

Note. A_a = Observed percentage area contributed by individual hyperfine pattern

A_c = Calculated percentage of iron ions on sublattices: tetrahedral against *a* and octahedral against *b* patterns.

is shown in Fig. 2. Because of the polycrystalline nature of the samples and low density of the pellets (65 per cent of X-ray density), the resistivities have no absolute significance, but the relative variation is meaningful.

4. DISCUSSION

(a) Analysis and interpretation of Mossbauer spectra

The spectra of samples with $x = 0.2$ and

$x = 0.4$ are similar to that of Fe_3O_4 . A comparison of the percentage areas of the individual Zeeman patterns *a* and *b* with the percentage of iron ions on octahedral and tetrahedral sites (see Table 2) suggests that the pattern *a* is due to all the tetrahedral ferric ions and *b* is due to all the octahedral ferrous and ferric ions. This appears to be approximately true when $x = 0.6$ except that a small fraction of iron ions give rise to a quadrupole

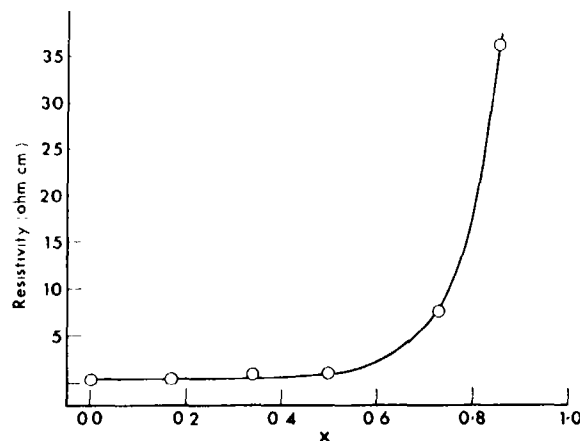


Fig. 2 Variation of resistivity in the system $\text{Zn}_2\text{Fe}_{1-x}\text{O}_4$ with composition at room temperature.

pattern. This indicates that, for $x \leq 0.6$, rapid electron hopping is occurring among all octahedral sites, rendering them indistinguishable.

In a spinel each octahedral cation has six occupied tetrahedral sites as near neighbours. Exchange interaction with the ions occupying these sites determines the hyperfine field at the nucleus of the octahedral cation. The electron density at the nucleus of this cation is also likely to be dependent on the nature of the tetrahedral near neighbours. Hence the reason why the Zeeman pattern *b* appears composite for $x > 0$ is that all the octahedral cations are not then surrounded by the same group of tetrahedral cations.

With any value of x , different fractions of octahedral cations will be surrounded by different numbers of near-neighbour tetrahedral cations which are ferric because of the random distribution of zinc and ferric ions among the tetrahedral sites. Each of these fractions will then give rise to its own hyperfine pattern. A similar explanation has been given[12] to explain the spectra of cobalt ferrite quenched from high temperature ... that some of Co^{2+} ions occupy tetrahedral sites. This explanation seems more convincing if we consider the spectrum of the sample with $x = 0.6$. At this high value of x , a significant fraction of octahedral cations will have too few near-neighbour tetrahedral cations which are magnetic to have ordered spins, and so will give rise to a quadrupole split spectrum. Such a pattern has been tentatively identified in the observed spectrum. As the value of x is increased further to 0.8, very few octahedral cations have a reasonably high number of near-neighbour magnetic cations in the tetrahedral sites, and so the Mössbauer spectrum shows only a quadrupole split pattern like that expected and observed for the sample with $x = 1$ [13]. The quadrupole splitting in ZnFe_2O_4 is due to the trigonal field on the octahedral sites[13]. A slight asymmetry in the shape and intensity of lines observed in the spectrum of the sample with $x = 0.8$ may be due to the presence of ferrous ions.

It is seen in Table 2 that the effective fields at the nuclei of iron ions, at both octahedral and tetrahedral sites ($H_{\text{eff}}(a)$ and $H_{\text{eff}}(b)$ respectively) decrease with increase in x . A likely explanation is the decrease in the strength of the inter-sublattice exchange interaction. The hyperfine field at a nucleus is believed to be proportional to the spontaneous magnetisation of the sublattice to which the nucleus belongs. In the present case, the two sublattice magnetisations oppose each other. The hyperfine field has been multiplied by the percentage of the total area represented by the corresponding patterns, and the differences (M_s), which should give a measure of the spontaneous magnetisation of the bulk material, has been plotted against x in Fig. 3. The form of the curve is very similar to that obtained by Gorter[14] for the variation of saturation magnetisation with x for similar systems. This supports the analysis of our Mössbauer spectra and their explanation.

associated with this electron hopping. A satisfactory theory to explain the mechanism of conductivity is yet to be developed. Rapid electron hopping would occur if some delocalisation of the 3*d*-orbitals of the cations in the octahedral sites gave rise to a metallic conduction band. But the temperature dependence of conductivity does not appear to be strictly metallic[15, 16], though these observations may be the result of minor imperfections or defects in the samples used. Recently workers in this field have tended to regard magnetite as metallic above the transition temperature[2, 4]. Our Mössbauer observations show that rapid electron hopping

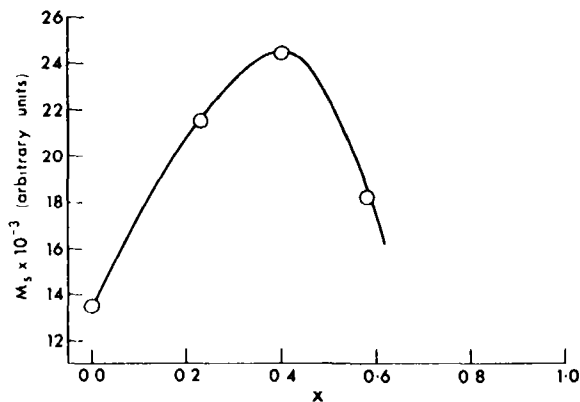


Fig. 3. Variation of the calculated spontaneous magnetisation (M_s) in the system $Zn_xFe_{3-x}O_4$ with composition at room temperature

involving all the octahedral cations continues in the present system up to a value of $x = 0.6$, and does not remain confined to pairs as in the case of non-stoichiometric magnetite [17]. Of course there are both cationic and anionic vacancies in the latter, and these may drastically affect the electron hopping and be responsible for the marked decrease in electrical conductivity. In our system, where there are no such vacancies, the metallic nature of conduction in Fe_3O_4 is therefore expected to continue up to about $x = 0.6$. The observed slow increase in electrical resistivity with x up to about $x = 0.6$ (see Fig. 2) is consistent with this. In the region $x \geq 0.8$, where magnetic ordering of spins is absent, hopping of electrons will occur in an uncorrelated manner, and so the conductivity is expected to be different in type. $ZnFe_2O_4$, with small deficiencies of Zn, and consequent presence of Fe^{2+} ions, is known to be an n -type semiconductor. It thus appears very likely that between $x = 0.6$ and $x = 0.8$, the system undergoes a transition from metallic to semiconductor type. The sharp increase in resistivity at around $x = 0.8$ (see Fig. 2) supports this hypothesis.

Electron hopping in magnetite is believed to occur through Zener double exchange [18],

but the mechanism of charge transfer is difficult to understand. Adler [2] has considered the hopping electrons to be in a $3d$ conduction band, but the magnitude of the drift mobility and the temperature dependence of conductivity do not conform to a band model. A narrow band mechanism with high effective mass due to polaron formation has been suggested by Mott and Austin [3]. In the presence of magnetic ordering electron hopping is likely to be highly correlated, and a large polaron model [4] to explain the conductivity mechanism up to $x = 0.6$ in the present system seems most reasonable. Beyond this, n -type semiconducting behaviour is due to uncorrelated electron hopping. But the possibility of a narrow-band mechanism cannot be discarded [19].

5. CONCLUSION

Mössbauer studies of the system $Zn_xFe_{3-x}O_4$ show that fast electron hopping among octahedral sites occurs up to $x = 0.6$. Metallic conductivity behaviour of Fe_3O_4 is therefore suggested to continue up to that composition. Beyond this, the system has n -type semiconducting behaviour. These conclusions are in agreement with the variation of resistivity in this system. Although

there is evidence for a large polaron model as the explanation of metallic conductivity for $x \leq 0.6$, more detailed conductivity studies on single crystals are needed to arrive at a definitive conclusion.

Acknowledgement – We wish to thank the Commonwealth Scholarship Commission in the U.K. for the award of a scholarship to M.M.R.

REFERENCES

1. BROESE VAN GROENOU A., BONGERS P. F. and STUYTS A. L., *Mater. Sci. Engng* **3**, 317 (1968/69).
2. ADLER D., *Solid St. Phys.* **21**, 1 (1968).
3. AUSTIN I. G. and MOIT N. F., *Adv. Phys.* **18**, 41 (1969).
4. GOODENOUGH J. B., *Czech. J. Phys.* **B17**, 304 (1967).
5. VERWEY E. J. W. and DE BOER J. H., *Rec. Trav. Chim.* **55**, 531 (1936).
6. NEEL L., *Ann. Phys.* **3**, 137 (1948).
7. VERWEY E. J. W. and HAILMANN E. L., *J. chem. Phys.* **15**, 174 (1947).
8. VERWEY E. J. W., HAAYMAN P. H. and ROMEIJN F. C., *J. chem. Phys.* **15**, 181 (1947).
9. BAUMINGER R., COHEN S. G., MARINOV A., OFER S. and SEGAL E., *Phys. Rev.* **122**, 1447 (1961).
10. ITO A., ÔNO K. and ISHIKAWA Y., *J. Phys. Soc. Japan* **18**, 1465 (1963).
11. ELIAS D. J., Thesis, Cambridge University (1968).
12. SAWATZKY G. A., VAN DER WOUDE F. and MORRISH A. H., *J. appl. Phys.* **39**, 1204 (1968).
13. MATHUR H. B., SINHA A. P. B. and YAGNIK C. M., *Indian J. Pure Appl. Phys.* **5**, 155 (1967).
14. GORTER E. W., *Nature, Lond.* **165**, 798 (1950). WENT J. J. and GORTER F. W., *Philips Tech. Rev.* **13**, 181 (1952).
15. MILES P. A., WESTPHAL W. B. and VON HIPPEL A., *Rev. mod. Phys.* **29**, 279 (1957).
16. CAI HOUN B. A., *Phys. Rev.* **94**, 1577 (1954).
17. DANIELS J. M. and ROSENCWAIG A., *J. Phys. Chem. Solids* **30**, 1561 (1969).
18. ROSENCWAIG A., *Can. J. Phys.* **47**, 2309 (1969).
19. AUSTIN I. G., SPRINGTHORPE A. J., SMITH B. A. and TURNER C. F., *Proc. Phys. Soc.* **90**, 157 (1967).

THE LOW-TEMPERATURE SPECIFIC-HEATS OF SEVERAL PALLADIUM-RICH PALLADIUM-ANTIMONY ALLOYS*

PAUL J. TSANG

Michigan State University East Lansing, Mich. 48823 and
IBM, East Fishkill Facility, Hopewell Junction, N.Y. 12533, U.S.A.

and

J. B. DARBY, Jr.

Argonne National Laboratory Argonne, Ill. 60439, U.S.A.

(Received 6 February 1970)

Abstract—The low-temperature specific-heat coefficients γ and the corresponding Debye temperatures θ were determined for four palladium-rich terminal solid-solution alloys containing 3, 6, 9 and 12 at.% antimony. The specific-heat results can be correlated with the room-temperature magnetic susceptibility and the vacant d -states of palladium decrease as the solute concentration increases but at a reduced rate when compared with noble metal-palladium systems. Comparison with Mossbauer results obtained over the same concentration range of the palladium-antimony system and optical data on noble metal-palladium alloys suggest that a screening model, in which each atomic cell is electrically neutral, is a more appropriate description than a charge transfer model.

1. INTRODUCTION

THE ELECTRONIC structure of several binary palladium alloys has been investigated extensively by a variety of techniques. These alloys are of interest because pure palladium has a nearly filled d -band, with high density of states at the Fermi level, that decreases rapidly as noble metals or polyvalent solute atoms are dissolved in palladium. Thus, several macroscopic properties of palladium alloys, such as the magnetic susceptibility and electronic specific heat, show large variations with composition and provide a definitive basis for the comparison of experimental results among the various palladium-base alloy systems.

A large quantity of magnetic susceptibility data are available on palladium alloys. The susceptibility results for a variety of binary systems (including Pd-Ag[1], Pd-Au[2], Pd-Cu[3], Pd-Al[4], Pd-Cd[5], Pd-In[6], Pd-Sb[5], and Pd-Sn[7]) lie more or less on a common curve, when plotted as a function of

the electron concentration e/a . The rate of change of the susceptibility is approximately proportional to the

Electronic specific-heat measurements have been made on only a few of the palladium alloys, i.e. the complete series of solid solutions in the Pd-Ag system[1], the 5.2 at.% Sn in palladium[8], and a few alloys in the Pd-Th and Pd-U systems[8]. When the electronic specific-heat coefficient γ is plotted vs. electron concentration e/a for the alloys in the four systems, a common curve is obtained when effective valencies of 4, 4 and 6 are assigned to tin, thorium, and uranium, respectively. The γ values for the Pd-Ag system[1] decrease abruptly to low values at the same e/a ratio at which the d -holes in Pd are filled,

*Work performed under the auspices of the U.S. Atomic Energy Commission.

as indicated by the susceptibility results. A rigid-band interpretation for the various properties of palladium-base alloys appears to be inadequate in view of theoretical calculations [9] of the electron-magnon interactions and recent de Haas-van Alphen measurements on pure palladium [10]. Thus, experimental γ values give only a qualitative indication of the variation of the density of states of alloys with composition, and an accurate assessment of the various interactions are required to obtain the true density-of-states curve. The experimentally determined Fermi surface of palladium from Vuillemin's measurements [8], confirmed by the calculations of Mueller and Priestley [11], clearly indicate that the d -band of palladium contains 0.36 holes rather than the 0.6 hole predicted from rigid-band arguments.

While a theoretical basis for relating thermodynamic properties, such as heats of formation, to the electronic structure of alloys does not exist, a correlation between the electronic structure and the heats of formation has been suggested for a few alloy systems [12]. The heats of formation ΔH_f at 298°K were determined for the palladium-rich solid solutions in the Pd-Cd, Pd-In, Pd-Sn and Pd-Sb systems [13]. When the heats-of-formation values are plotted as a function of electron concentration e/a (assuming the group valence for the solutes), the values for the systems containing the solutes Cd, In, or Sn lie essentially on a common curve, while the Pd-Sb values are substantially above the curve. It has been observed [14] that antimony does not always display the group valence of five in compounds. Also, the room-temperature magnetic susceptibility vs. e/a curve for palladium-rich Pd-Sb terminal solid-solution alloys [5] deviates from the curve for the Pd-Ag system above 5 at.% antimony. Low-temperature specific-heat data for the Pd-Sb system were not available to compare with the trend observed in the susceptibility results.

The present investigation was initiated to determine if the γ values for the palladium-rich

Pd-Sb alloys would superimpose on the γ vs. e/a curve for Pd-Ag alloys derived from low-temperature specific-heat measurements.

2. EXPERIMENTAL TECHNIQUES

The low-temperature specific-heat measurements were made on four palladium alloys containing 3, 6, 9 and 12 at.% antimony, respectively. To compensate for the reduction in specific heat as the antimony concentration increased, the specimen mass appropriate for low-temperature calorimetry studies varied from approximately 37 g for the 3 at.% antimony alloy to 113 g for the 12 at.% alloy. The alloys were prepared by arc-melting the requisite amounts of 99.99 + % pure palladium and 99.995% pure antimony on a water-cooled copper hearth in a helium-argon atmosphere. Several of the individual buttons produced by arc melting (mass of 15–20 g each) were charged into a high-purity recrystallized alumina crucible and remelted in an induction furnace under a high-purity (99.999%) argon atmosphere to produce an ingot approaching a right-circular cylinder. The ingot was completely enclosed in an envelope of molybdenum foil, sealed in an evacuated quartz capsule, and annealed at 1000°C for 24 hr; followed by an anneal at 1100°C for 72 hr to continue the homogenization process. The annealing was terminated by a water quench without breaking the capsule. The ingot was then machined, without any lubricants, into a three-quarter-inch diameter right-circular cylinder. All surfaces were ground with emery paper to remove surface contamination, cleaned in acetone, and given a final rinse in alcohol. A strain-relief anneal followed for 1 hr at 1100°C and the specimen was furnace cooled to room temperature. A metallographic examination confirmed that the alloys consisted of a single phase and were free of segregation.

The low-temperature specific-heat measurements were carried out between 1.4 and 4.2°K in a ^4He cryogenic facility [15]. Each alloy ingot was cut into two specimens of equal

volume. One surface of each specimen was ground and polished to ensure good thermal contact with the heater-thermometer assembly. The sample and heater-thermometer assembly configuration was similar to that described by Wei *et al.* [16].

A semiconducting carbon resistor, with a nominal resistance of 60 Ω at room temperature, was employed as a thermometer. The thermometer was calibrated against the NBS (1958) ^4He Temperature Scale prior to each experiment, and the data were fitted to the equation

$$(\ln R/T)^{1/2} = A + B \ln R. \quad (1)$$

The coefficients A and B , determined by the least-squares method, were -1.006643 and 0.624630, respectively. The maximum root-mean-square deviation of the experimental points from the thermometer calibration curve, fitted to equation (1), is 0.05 per cent, while the maximum total calibration error is less than 1.5 per cent [17].

3. RESULTS

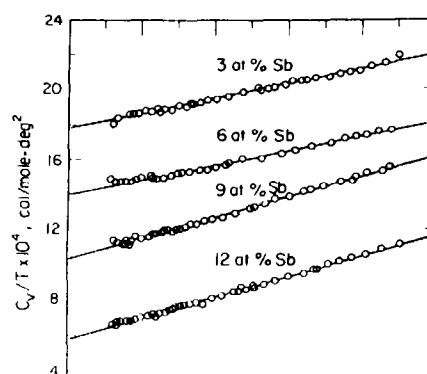
At least 40 heat-capacity values were determined for each alloy between 1.4 and 4.2 K and gave a good fit to the heat-capacity equation

$$C_p/T = \gamma + \beta T^2.$$

By extrapolation of a least-squares fit of the experimental C_p/T vs. T^2 curves to absolute zero, the electronic specific-heat coefficients γ for the four alloys were obtained, and the corresponding Debye temperatures θ were calculated from the slope of the curves. The γ and θ values are tabulated in Table 1 and the C_p/T vs. T^2 curves are shown in Fig. 1. In Fig. 2, the electronic specific-heat coefficients γ for the Pd-Sb alloys are plotted as a function of electron concentration e/a . The e/a ratio for a given alloy was obtained by assuming that the total number of 5s and 5p electrons of Sb contributed to the alloy was five.

Table 1. Values of the electronic specific-heat coefficient and the Debye temperature of palladium-rich Pd-Sb alloys

Alloy composition (at.% Sb)	$\gamma \times 10^4$ (cal/mole-deg ^{2})	θ ($^\circ\text{K}$)
3	17.78	280.1
6	13.86	278.6
9	10.21	249.1
12	5.78	250.2



4. DISCUSSION

The assumption that the five conduction electrons of antimony are transferred to the empty d holes in palladium may not be valid, since the γ values for the Pd-Sb alloys lie above the γ vs. e/a curve for the Pd-Ag system; although the general trend that γ decreases as the solute concentration increases is noted for both the Pd-Ag and Pd-Sb values. If the γ values from the present measurements are superimposed on the curve for the Pd-Ag system, the number of electrons of antimony transferred can be inferred, neglecting en-

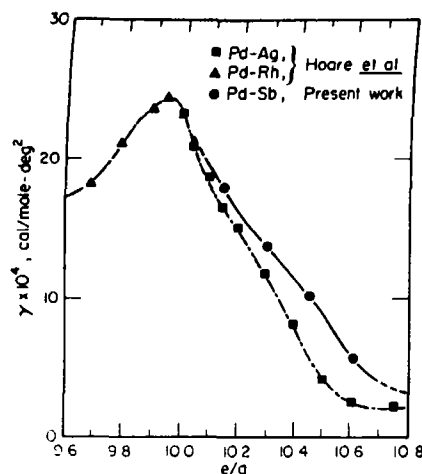


Fig. 2 Electronic specific-heat coefficients versus electron concentration for palladium-rich Pd-Sb and Pd-Rh alloys and for the Pd-Ag binary system.

hancement effects, by projecting the experimental values onto the abscissa. The extrapolation indicates that approximately 3.7 electrons would be transferred. Although the value derived from the extrapolation is not exact, since interactions that may enhance the γ quantities have been ignored, the apparent number of conduction electrons of antimony that would participate in a charge-transfer interpretation would be less than five. Hence, the specific-heat measurements appear to correlate with the observations from magnetic-susceptibility studies.

Magnetic susceptibility measurements have been carried out on the palladium-rich solid solutions of the Pd-Cd[5], Pd-In[6], Pd-Sn[7], and Pd-Sb[5] systems. The susceptibility results for the Pd-Ag and Pd-Cd alloys superimpose essentially on a common curve when plotted as a function of electron concentration. The remaining three systems also lie on the same general curve (assuming rigid-band behavior) up to approximately 8.8, 5.5 and 2.6 at.% indium, tin, or antimony, respectively, and then progressively deviate from the curve as the solid-solubility limit is approached. The deviations indicate that the 'apparent valency' of the three solutes decreases, with concen-

tration, from the valence assigned according to the group number in the periodic table. In order for the susceptibility values to coincide with the Pd-Ag values at higher concentrations, the apparent valence of tin or antimony would be approximately three or four, respectively. In terms of the electronic state of free atoms, the three polyvalent solutes indium, tin, and antimony are likely to display p -like as well as s -like character, and Harris *et al.*[7] have suggested that the susceptibility deviations may indicate the formation of localized p states.

A model has been proposed by Montgomery *et al.*[8] for palladium alloys, with noble or polyvalent elements as solutes, that provides an interesting alternative to the requirement of charge transfer for the rigid-band model. It is assumed that every atomic cell in an alloy is electrically neutral and differences in the nuclear charges are essentially screened by the itinerant electrons,* i.e. a charge of Z -conduction electrons is associated with a solute site. The effect of a polyvalent solute 'is to induce the palladium matrix to convert some of its own s electrons into d electrons' until the number of d holes in palladium decreases to zero at an e/a ratio of approximately 0.6. The model is attractive in that it is not necessary to correlate the critical e/a ratio with the number of d holes in elemental palladium, nor the solute valency Z with the rate at which the d band fills. Therefore, the model is consistent with the de Haas-van Alphen results that indicate 0.36 d holes in pure palladium, and with the abrupt changes observed at the critical e/a ratio in the average properties, such as specific heats and magnetic susceptibilities.

Some information has been obtained on the conduction-electron density at tin (^{119}Sn) or

*Experimental justification is the fact that the tetragonal phase (α') in the palladium-rich Pd-Cd system reverts to a face-centered-cubic modification by mechanical working of the alloy[18]. Also, the compound Pd_3In has a face-centered-tetragonal structure that can be converted to a face-centered-cubic form by deformation[19]. Hence, the ordering energy is much smaller than the Madelung energy in an ionic crystal.

antimony (^{121}Sb) nuclei in binary palladium alloys from the isomer shifts in the Mössbauer spectra [7, 20]. The isomer shifts are derived from a change in the charge radius of the nucleus when a γ -ray is emitted and the shifts vary linearly with the electron density at the nuclear site. Harris and Cordey-Hayes [7] reported negative values for the ^{119}Sn isomer shifts for the palladium-rich solid solutions that indicate $5s$ -electron density about the tin nuclei is less than in β -Sn, and suggested the results are consistent with a simple rigid-band model. Montgomery and Ruby [20] measured the isomer shifts in palladium-rich Pd-Sb alloys and found a close correlation with the Pd-Sn results. If a charge-transfer interpretation is applied, the 'apparent valency' of antimony in the Pd-Sb alloys is somewhat less than 4. However, Montgomery and Ruby [20] qualitatively explain the isomer shifts for the Pd-Sb and Pd-Sn alloys in terms of a screening model. To a first approximation each atomic cell in the alloys is electrically neutral as suggested by Friedel's theory [21], and the d -band level of palladium is filled by the conversion of s electrons into d electrons within the palladium cells. However, the mechanism by which the solute perturbs the d band of palladium remains unresolved.

Further support for the screening model of Montgomery and Ruby is found in the measurements of the optical absorption spectrum by Myers *et al.* [22] in alloys of palladium in copper, silver, or gold. The results show that the d -electrons of both silver and palladium atoms in silver-palladium alloys may be considered as occupying bound states over the entire composition range and no significant overlap occurs either in energy or space, contrary to the requirements of a rigid-band model. The distribution of conduction-electron charge density was very nonuniform and associated totally with the silver atoms in alloys containing less than 40 at.% palladium.

In summary, the electronic specific-heat coefficients and the magnetic susceptibility

results show a correlation between the rate at which the d band fills and the solute valency in palladium-antimony alloys. The correlation is, at most, qualitative and it appears that a screening model, in which the solute atoms are nearly perfectly screened by conduction electrons, is compatible with the measurements of various properties of palladium alloys.

Acknowledgements—The authors are indebted to Dr. C. T. Wei, Michigan State University, for providing the experimental facilities and for fruitful discussions. Mr. Paul Paulikas provided experimental assistance in the preparation of the alloys. We thank Dr. H. Montgomery and Dr. F. M. Mueller for useful discussions and suggestions.

REFERENCES

- HOARE F. E., MATTHEWS J. C. and WALLING J. C., *Proc. R. Soc. A* **216**, 502 (1953); HOARE F. E. and YATES B., *Proc. R. Soc. A* **240**, 42 (1957).
- VOGT E., *Ann. Phys.* **14**, 1 (1932).
- SVENSSON B., *Ann. Phys.* **14**, 699 (1932).
- GERSTENBERG D., *Ann. Phys.* **2**, 236 (1958).
- LAM D. J. and MYLES K. M., *J. phys. Soc. Japan* **21**, 1503 (1966).
- HARRIS I. R., NORMAN M. and BRYANT A. W., *J. less-common Metals* **16**, 427 (1968).
- HARRIS I. R. and CORDEY-HAYES M., *J. less-common Metals* **16**, 333 (1968).
- PAULING L., *The Nature of the Chemical Bond*, Cornell University Press, New York (1960).
- For details of the system see WEI C. T., Ph.D. Thesis, University of Illinois 1958, and TSANG P. J. and WEI C. T. (To be published).
- WEI C. T., CHANG C. H. and BECK P. A., *Phys. Rev.* **120**, 426 (1960).
- TSANG P. J., Ph.D. Thesis, Michigan State University (1968).
- PRATT J. N., MYLES K. M., DARBY J. B. Jr. and MUELLER M. H., *J. less-common Metals* **14**, 427 (1968).
- PRATT J. N., University of Birmingham, Birmingham, England (private communication).
- MONTGOMERY H. and RUBY S., *Phys. Rev.* **B1**, 2948 (1970).
- FRIEDEL J., *Adv. Phys.* **3**, 446 (1954).
- MYERS H. P., WALLDEN L. and KARLSSON A., *Phil. Mag.* **18**, 725 (1968).

COVALENCY PARAMETERS FOR Cr^{3+} , Fe^{3+} AND Mn^{4+} IN AN OXIDE ENVIRONMENT

B. C. TOFIELD and B. E. F. FENDER

Inorganic Chemistry Laboratory, University of Oxford, England

(Received 3 February 1970)

Abstract—Magnetic moment reduction in the perovskites LaCrO_3 , LaCrO_3 , YFeO_3 and CaMnO_3 have been determined by neutron diffraction measurements. The results analysed in terms of covalency parameters are, LaFeO_3 , $f_\sigma + 2f_\pi + f_\kappa = 10.0 \pm 0.5\%$; YFeO_3 , $f_\sigma + 2f_\pi + f_\kappa = 11.0 \pm 1.0\%$; LaCrO_3 , $f_\pi = 1.6 \pm 0.6\%$; CaMnO_3 , $f_\pi = 3.3 \pm 0.8\%$. For the d^1 ions discrepancies between f_π determined by neutron and resonance methods are explained in terms of spin polarisation effects and revised estimates of $f_\pi = 2.7 \pm 0.6\%$ (LaCrO_3) and $f_\pi = 5.3 \pm 0.8\%$ (CaMnO_3) are presented. Consideration of charge transfer suggests $f_\sigma + f_\kappa$ is about 3.0% in LaCrO_3 .

1. INTRODUCTION

Atomic magnetic moments in antiferromagnetically ordered solids can be interpreted in terms of covalency parameters related to a simple molecular orbital description of bonding in the solid [1, 2]. Recent use of neutron diffraction techniques to measure the reduction in observed moment from that expected for a fully ionic lattice has enabled the change in covalency parameter to be evaluated in a series of manganese compounds (MnO , MnS [3], MnSe , [4]).

The present study on a series of oxides has been carried out in order to gain insight into the change in covalency as the oxidation state of the metal ion increases. Four mixed oxides in which the transition metal ion is octahedrally co-ordinated to O^{2-} have been studied: LaCrO_3 ($\text{Cr(III)}d^3$ ion), CaMnO_3 ($\text{Mn(IV)}d^3$ ion), LaFeO_3 and YFeO_3 ($\text{Fe(III)}d^5$ ion). Two of these oxides, LaCrO_3 and LaFeO_3 , have been investigated by Nathans *et al.* [2] and their results provide an important indication of the covalency to be expected. We have, however, noted earlier [5] that variations in stoichiometry may affect the observed moment reduction so that in carrying out the present detailed investigation we have paid particular attention to the

characterisation of the compounds studied.

The molecular orbital model used takes into account only overlap of metal d orbitals with $2s$ and $2p$ orbitals of oxygen. The appropriate antibonding wave functions for the octahedral environment are:

λ_π are admixture parameters. In an antiferromagnetic solid where the spin on the ligand is fully cancelled, the effective spin quantum number S , determined by neutron diffraction is readily shown to be:

$$S/S_0 = 1 - 4\lambda_\pi^2 \quad \text{for a } d^3 \text{ ion (as } K \rightarrow 0) \quad (2)$$

and

$$S/S_0 = 1 - 1.2(\lambda_\sigma^2 + 2\lambda_\pi^2 + \lambda_\kappa^2) \quad \text{for a } d^5 \text{ ion (as } K \rightarrow 0)$$

where S_0 is the spin quantum number for a fully ionic lattice and K is the scattering

vector. The covalency parameters (A^2) are simply related to λ as follows:

$$A_{\sigma}^2 = \frac{1}{3}\lambda_{\sigma}^2, A_s^2 = \frac{1}{3}\lambda_s^2 \text{ and } A_{\pi}^2 = \frac{1}{4}\lambda_{\pi}^2. \quad (3)$$

NMR[6, 7] and EPR[7, 8] studies also allow determination of covalency parameters by measurement of the amount of spin transferred to the ligand. A spin transfer coefficient f is usually defined as the fractional spin transferred to each ligand orbital when the metal orbitals are each singly occupied in which case:

$$f_{\sigma} = \frac{1}{3}N_{\sigma}^2\lambda_{\sigma}^2, f_s = \frac{1}{3}N_s^2\lambda_s^2 \text{ and } f_{\pi} = \frac{1}{4}N_{\pi}^2\lambda_{\pi}^2. \quad (4)$$

It is obvious therefore that when the degree of approximation is the same in both methods (i.e. powers of λ and the overlap integral higher than two are neglected) $N_{\sigma} = N_{\pi} = 1$ and $A_{\sigma}^2 = f_{\sigma}$ etc.

The resonance methods depend on the ligand having a non-zero nuclear spin. For oxides $I(^{16}\text{O}) = 0$ and there appears to be only one measurement (on MnO) with ^{17}O enriched samples[9].

In comparing results (see Discussion) from neutron and resonance techniques it is important to note that though both methods measure f_{π} (or A_{π}^2) for a d^3 ion, for d^5 ions the resonance techniques measure f_s and $f_{\sigma} - f_{\pi}$ (c.f. equation (2)).

2. EXPERIMENTAL

Sample preparation and analysis

(a) LaFeO_3 was prepared from the precipitated ferricyanide as described by Gallagher [10]. A saturated solution of 'Analar' potassium ferricyanide was added to an equivalent quantity of warm neutral chloride prepared by dissolving La_2O_3 (Koch-Light Laboratories Ltd., purity 99 per cent) in hydrochloric acid. The precipitate of lanthanum ferricyanide was dried, heated to 600°C and then fired

in air at 1050°C . X-ray powder photographs taken with a Guinier focussing camera (copper K_{α} radiation) showed no impurity lines. The orthorhombic lattice parameters obtained agreed with those of Geller and Wood[11]: $a = 5.556 \text{ \AA}$, $b = 5.565 \text{ \AA}$, $c = 7.862 \text{ \AA}$. The determination of ion (IV) in the sample was carried out using a modification of the method of Mori *et al.*[12]. The mixed oxide was dissolved in acidified standard ferrous solution under flowing argon and ferric iron determined with E.D.T.A. at pH 2 using thiosalicylic acid as indicator and glycine as a buffer. Total iron was determined similarly (after persulphate oxidation) to give a final analysis of $\text{LaFeO}_{3.02 \pm 0.01}$.

(b) YFeO_3 was prepared and analysed in a similar manner to LaFeO_3 (using Johnson Matthey Ltd. 'Specpure' Y_2O_3) except that the temperature of the final ignition was 1200°C . The X-ray photograph (Guinier camera) gave only lines expected for YFeO_3 and the d -spacings agreed with those given by Eibschutz[13]; $a = 5.283 \text{ \AA}$, $b = 5.592 \text{ \AA}$, $c = 7.603 \text{ \AA}$. Chemical analysis indicated a stoichiometric oxide of $\text{YFeO}_{3.00 \pm 0.01}$.

(c) LaCrO_3 was prepared by reaction of equimolar quantities of La_2O_3 and Cr_2O_3 in air at 1550°C . Both oxides which were supplied as 'Specpure' chemicals by Johnson Matthey Ltd. were mixed in a ball-mill before being pressed into pellets ($2.5 \times 10^3 \text{ kg per cm}^2$). The mixture was fired once for 6 hr and then reground, pressed and heated again for a further period of 6 hr. No impurity lines were observed on a Guinier photograph and the lattice parameters obtained were in agreement with those reported by Geller[14]: $a = 5.477 \text{ \AA}$, $b = 5.514 \text{ \AA}$, $c = 7.755 \text{ \AA}$. No change in weight was observed on firing indicating a stoichiometric oxide $\text{LaCrO}_{3.00}$. An emission spectrographic search was made for iron, aluminium and silicon, the most likely impurities to have been incorporated during the preparations, but significant quantities ($>100 \text{ ppm}$) were not detected.

(d) CaMnO_3 was prepared by direct re-

action of Mn_2O_3 and CaCO_3 supplied as 'Specpure' chemicals by Johnson Matthey Ltd. below 1100°C . The mixed oxide which resulted was heated for 60 hr in air at 1000°C , reground, pressed into pellets and heated for 48 hr in flowing oxygen at 1050°C , and finally (after re-grinding and pressing again) for 48 hr at 750°C in oxygen. This sample (sample *A*) showed two very faint impurity lines on X-ray photographs with the Guinier camera (using strictly monochromatic copper $K_{\alpha 1}$ radiation). Sample *A* was reheated for 120 hr at 600°C under 700 atm. oxygen. Subsequent X-ray examination of the new sample (sample *B*) showed that one of the impurity lines had disappeared. The impurity lines were not visible in neutron diffraction patterns and both samples were used in covalency determinations. CaMnO_3 has been indexed as cubic with a lattice parameter double the primitive cell size of $3.729 \text{ \AA}$ [15]. The compound is, however, probably orthorhombic as splittings of the (422) and (440) cubic lines were detected. These splittings do not quite correspond with the orthorhombic parameters [16] of $a = 5.270 \text{ \AA}$, $b = 5.270 \text{ \AA}$, $c = 7.464 \text{ \AA}$ for $\text{CaMnO}_{2.98}$ but for purposes the error is small. The power of the samples was determined by oxidation of iodide to give a stoichiometric $\text{CaMnO}_{2.99 \pm 0.01}$ for both samples though there was some indication that the oxygen content was slightly higher for sample *B* than for sample *A*.

Neutron diffraction

Experiments were carried out on the powder diffractometer in DIDO reactor at A.E.R.E., Harwell, the samples being contained in thin-walled aluminium cans.

G-type magnetic ordering is observed for all four compounds. A perfectly cubic magnetic lattice with this type of ordering and a cell side twice that of the primitive perovskite cell has magnetic peaks allowed only for h, k, l all odd. The magnetic symmetry of the compounds studied is in fact orthorhombic,

however, the unit cell being the same size as the crystallographic cell with reflections allowed if $(h+k)$ and l are both odd. For pseudocubic symmetry where the orthorhombic cell parameters are related by $c = 2a = 2b$ these two descriptions are equivalent, but when the degeneracy is removed, splitting of the magnetic peaks occurs, the cubic (111) for example, becoming the orthorhombic (011) and (101). Such splitting was not observed for LaFeO_3 , LaCrO_3 and CaMnO_3 where the distortions are very small, but could be seen for the more distorted YFeO_3 with the (011) peak about three times the intensity of the (101). This indicated the antiferromagnetic spin axis to be along the [100] direction, agreeing with single crystal magnetisation data [17, 18]. This spin direction was assumed in calculation of the magnetic structure factors not only for YFeO_3 but also for the other three compounds. The shape of the unresolved peaks in the latter oxides gave some indication that the (011) peak was larger than the (101) but in any case the sum of structure

factor uncertainties in the atomic positional parameters. The (111) reflection of powdered germanium (supplied as 'Specpure' element by Johnson Matthey Ltd.) mixed with the oxide was used therefore as an external calibrant.

The major error in determining the intensity of the Bragg peaks arises not from statistical counting errors but from imperfect sample alignment. Several runs with the sample at different orientations to the neutron beam were carried out on each compound. All intensity measurements used to determine covalency parameters were made at 4.2°K .

Peak intensities, which varied between 20,000 and 50,000 counts, were obtained by summing the total counts across the peak (taken at 0.04° or 0.06° intervals) after subtraction of the flat background. The latter was obtained by averaging the counts over 1° on each side of the peak. The peaks investigated were well resolved except for slight overlap of the small YFeO₃ (111) nuclear peak with the germanium (111) reflection. The former peak was however accurately estimated by comparison with other YFeO₃ nuclear peaks and the ratios previously determined from neutron diffraction patterns for pure YFeO₃. CaMnO₃ sometimes showed two small additional peaks (below 2θ = 25°) at 4.2°K, presumably arising from a new low temperature phase. One of these peaks overlapped the Ge (111) reflection but the extent of this contribution to the (111) peak was readily estimated from an intercomparison of nuclear peaks on samples with and without the presence of germanium.

3. TREATMENT OF RESULTS

The standard expression for the intensity of a Bragg peak (*I*) from a cylindrical polycrystalline sample is

$$\frac{I}{I_0} = \frac{kVj_{hkl}N_c^2|F_{hkl}|^2e^{-2W}A(\theta)}{\sin \theta \sin 2\theta} \quad (5)$$

where *I*₀ is the incident neutron flux, *k* a constant for the apparatus, *V* is the sample volume, *j*_{hkl} is the multiplicity of the reflection, *N*_c is the number of unit cells per unit volume, *F*_{hkl} is the structure factor, *θ* is the Bragg angle, *e*^{-2*W*} is the Debye-Waller factor and *A*(*θ*) is the absorption factor.

For the ABO₃ perovskites studied the theoretical ratio of (001) + (101) magnetic peak intensity to the germanium (111) peak (*I*_{Ge}) is

$$\frac{I_{ABO_3}}{I_{Ge}} = 1.389 \times 10^{-22} \frac{m_{ABO_3}}{m_{Ge}} \cdot \frac{g^2/4 \langle S_z \rangle^2}{M_{ABO_3} V_{cABO_3}}$$

$$\times \left[\frac{\langle q^2 \rangle_{011} |f(K)|_{011}^2}{\sin \theta \sin 2\theta_{011}} + \frac{\langle q^2 \rangle_{101} |f(K)|_{101}^2}{\sin \theta \sin 2\theta_{101}} \right]_{ABO_3} \times \frac{A(\theta)_{101+011}}{A(\theta)_{111}} \times e^{2(W_{Ge} - W_{ABO_3})} \quad (6)$$

where *m* is the mass of sample taken, *g* is the transition ion *g*-factor, *⟨S_z⟩* the expectation value of the transition ion spin, *M*_{ABO₃} the molecular weight of the perovskite, *V*_{cABO₃} the unit cell volume of the perovskite, *⟨q²⟩* the orientation factor for a magnetic reflection, [19] and *f*(*K*) the magnetic form factor. The numerical term involves quantities constant for all the compounds, and the following values were taken: *j*_{ABO₃} = 4, *j*_{Ge} = 4, *M*_{Ge} = 72.59, *b*_{Ge} = 0.84 [20], *g*_{ABO₃} = 4, *g*_{Ge} = 8, *V*_{cGe} = 5.6576 × 10⁻²⁴ cm³ [21], *sin θ sin 2θ*_{Ge} = 0.05132, and (e²γ/*mc*²)² = 0.2906 × 10⁻²⁴ cm², where *b*_{Ge} is the scattering length of germanium and *g* is the number of formula units per unit cell. *⟨S_z⟩* is less than the spin quantum number *S* because of the zero-point spin deviation of an antiferromagnet [22]. The values of *⟨S_z⟩* given by Davis [23] were used.

The observed value of *I*_{ABO₃}/*I*_{Ge} divided by the calculated ratio gives the reduction in the intensity of the magnetic peaks, and hence in the magnetic moment, arising from covalency. Before application of equation (6) however a number of corrections had to be considered. The orthorhombic space group Pbnm allows a small nuclear contribution to the (101) intensity which must be subtracted from the observed (011) and (101) combined peak. Room temperature diffraction patterns for LaCrO₃ (*T*_v = 282°K) [24] and CaMnO₃ (*T*_v = 123°K) [16] showed that the nuclear intensity is negligible for CaMnO₃ and less than 2 per cent of the total magnetic intensity in LaCrO₃. The (101) nuclear peak intensity of YFeO₃ (*T*_v = 640°K) [25] was estimated from the atomic positional parameters given by Coppens and Eibschutz [26]. For LaFeO₃ (*T*_v = 740°K) [25] reasonable agreement was

obtained between observed and calculated nuclear peak intensity ratios by assuming perfect octahedral co-ordination of oxygen about the iron atoms and an Fe–O distance of 2.01 Å. The estimated (101)_{nuclear} contributions to the total peak were 1 per cent (YFeO₃) and 1.5 per cent (LaFeO₃) and these corrections were made to the observed intensities.

The compounds all display parasitic ferromagnetism which will reduce the antiferromagnetic sublattice magnetisation. The published values of the canting angles [25, 27, 28] indicate however that the correction to the magnetic intensity must be less than 0.1 per cent. All peaks were corrected for a half wavelength contribution. This was generally less than 1 per cent.

In equation (6) the Debye–Waller term was estimated using the zero-point formula

$$2W = (5740/\bar{A}\Theta) \sin^2 \theta/\lambda^2 \quad (7)$$

where λ , the neutron wavelength is in angstrom units and $\bar{A}$ is the mean atomic weight. Debye temperatures of 362°K [29] for germanium and 800°K [25] for the perovskites were used. This term affects the magnetic peak intensity by about 0.2 per cent and the germanium reflection by 0.5 per cent. Absorption was small and essentially independent of wavelength and was ignored.

Free ion form factors were used [30].

form factor for Mn⁴⁺ has not been published but it was estimated to lie between 0.893 and 0.905 at the (011) and (101) reflection of CaMnO₃. This uncertainty has been incorporated into the final error.

4. RESULTS AND DISCUSSION

The results obtained using equations (2) and (6) are given in Table 1.

Uncertainties in covalency parameters

The principal uncertainties are associated with the magnitude of the zero-point spin deviation and with the form factor. The calculated values of the zero-point spin deviation are probably at least as accurate as any experimental determinations for the reasons discussed by Owen and Taylor [31]. The different theoretical values vary slightly however and Davis [23] showed that the reduction will be considerably decreased if there is significant anisotropy. Davis did not discuss the Dzialoshinskii [32] anisotropy responsible for the spin canting in the compounds. The form factor for Mn⁴⁺ has not been published but it was estimated to lie between 0.893 and 0.905 at the (011) and (101) reflection of CaMnO₃. This uncertainty has been incorporated into the final error.

Table 1. Covalency parameters

	$I_{(011) + (101)}^{\text{exptl}} / I_{\text{Ce}}$	$I_{(011) + (101)}^{\text{calc}} / I_{\text{Ce}}$	S / S_0	$f_{\pi} + 2f_{\tau} + f_{\sigma}$	f_{π}
LaFeO ₃ ^a	0.615 ± 0.009	0.793	0.881 ± 0.006	10.0 ± 0.5%	—
YFeO ₃ ^b	0.882 ± 0.025	1.172	0.868 ± 0.012	11.0 ± 1.0%	—
LaCrO ₃ ^b	0.333 ± 0.017 ^c	0.379	0.936 ± 0.025	—	1.6 ± 0.6%
CaMnO ₃ ^d	(A) 0.676 ± 0.007 (B) 0.676 ± 0.008	0.849 ± 0.011 ^e 0.945 ± 0.013	0.869 ± 0.032	—	3.3 ± 0.8

^aFive determinations.

^bFour determinations.

^cError includes uncertainty in (101) nuclear intensity.

^dTwo determinations on sample A and three on sample B.

^eError includes uncertainty in form factor.

use of the free ion form factor in this compound has been shown to cause a change of about +0.5 per cent in the covalency parameters[3]. The form factors for d^5 ions may be contracted possibly because of some $4s$ contribution to the bonding[34]. However, the Fe^{3+} form factor[35] (for Fe^{3+} in Fe_3O_4) after scaling by the covalency parameters determined in this work, is close to the free ion value at $\sin \theta/\lambda \sim 0.1$ although significantly contracted at higher $\sin \theta/\lambda$. This supports the contention[2] that the use of free ion form factors will not introduce a large error when peaks at $\sin \theta/\lambda \sim 0.1$ are being measured.

The maximum uncertainty associated with the zero point deviation and the form factor is probably of similar magnitude to the experimental errors and should not qualitatively affect the conclusions discussed below.

Comparison with previous results

The covalency parameters obtained by Nathans *et al.*[2], for LaFeO_3 and LaCrO_3

(corrected for zero-point spin deviation) and those obtained in the present work are given in Table 2.

There are significant differences between the two sets of data but we have investigated all possible sources of error and consider our results reliable. The similarity of the results for LaFeO_3 and YFeO_3 gives confidence in the data for these compounds and the moment reduction for LaCrO_3 is similar to that determined for Cr^{3+} in Cr_2O_3 [36]. Also Bertaut *et al.*[25] have measured the moment reduction of several rare earth orthochromites and although the quoted figures vary considerably the average reduction is close to our value of LaCrO_3 .

Covalency in d^3 ions

The neutron results together with resonance data for Cr^{3+} and Mn^{4+} are given in Table 3. This comparison suggests initially that covalency in fluorides is much larger than in oxides contrary to normal expectation and the evidence of divalent compounds where the

Table 2. Comparison with previous results

	Covalency parameters	Reference[2]	This work
LaFeO_3	$f_\sigma + 2f_\pi + f_d$	8.1%	$10.0 \pm 0.5\%$
YFeO_3	$f_\sigma + 2f_\pi + f_d$	—	$11.0 \pm 1.0\%$
LaCrO_3	f_π	3.7%	$1.6 \pm 0.6\%$

Table 3. Experimental covalency parameters for Cr^{3+} and Mn^{4+}

Ion	Technique	Host	f_π	$M-L$ distance ($\text{\AA}$)
Cr^{3+}	Neutrons ^a	LaCrO_3	$1.6 \pm 0.6\%$	$\sim 1.97 \text{ \AA}$
	E.P.R. ^b	KMgF_3	$4.9 \pm 0.15\%$	$1.99 \text{ \AA}$
	N.M.R. ^c	K_2NaCrF_6	$4.9 \pm 0.8\%$	$1.93 \text{ \AA}$
Mn^{4+}	Neutrons ^a	CaMnO_3	$3.3 \pm 0.8\%$	$\sim 1.87 \text{ \AA}$
	E.P.R. ^d	Cs_2GeF_6	9.2%	$1.74 \text{ \AA}$

^aPresent work.

^bRef. [43].

^cSHULMAN R. G. and KNOX K., *Phys. Rev. Lett.* **4**, 603 (1960).

^dHEIMHOLZ L., GUZZO A. V. and SANDERS R. N., *J. chem. Phys.* **35**, 1349 (1961).

covalency parameters are similar: $\text{MnO} = 3.5\%$ [3], $\text{MnF}_2 = 3.3\%$ [37], $\text{NiO} = 3.8\%$ [3], and $\text{KNiF}_3 = 2.5\%$ [38] or 4.3% [39]. The likely explanation for this discrepancy is that the resonance and neutron techniques measure different quantities because of spin polarization. Exchange interactions can lead to small amounts of unpaired spin in e_g , and possibly $4s$ orbitals which are polarised parallel to the existing spin of the t_{2g} orbitals of chromium or manganese. Correspondingly, spin which is polarized in the opposite direction is left on the ligand. NMR and EPR studies which detect unpaired spin on the *ligand* thus indicate increased covalence whereas the neutron diffraction measurements show less than the normal reduction in spin. Spin polarization effects have been discussed by Owen and Thornley [7] and recently Berger *et al.* [40] and Stauss [41] have invoked spin polarization in Cr^{3+} containing spinels to account for NMR hyperfine fields.

If the net spin per ligand induced by spin polarization in the metal e_g and $4s$ orbitals is denoted by f'_σ the moment reduction measured by neutrons is $4f_\pi - 2f'_\sigma$ but the hyperfine interaction measures $-f'_\sigma - f_\pi$. To correct f'_σ in the absence of comparable oxide or fluoride data we have assumed that covalency parameters for fluorides and oxides are to a first approximation the same. Calculated values of corrected f_π are as given in Table 4. It is seen that with or without allowance for spin polarisation there is a large increase in π bonding in CaMnO_3 over LaCrO_3 .

Covalency parameters for Fe^{3+} , Mn^{2+} , Cr^{3+} (d^5 ions)

The assumption of similar covalency para-

meters for oxides and fluorides allows estimation of individual values of f_σ and f_π for Fe^{3+} and Mn^{2+} (cf. Nathans *et al.* [2]). An average value for LaFeO_3 and YFeO_3 was taken for the $\text{Fe}^{3+}-\text{O}^{2-}$ covalency to give individual parameters as follows:

$$\begin{aligned} \text{Mn}^{2+} \quad f_s &= 0.5 \pm 0.02\%, f_\sigma = 1.2 \pm 0.2\%, \\ &\quad f_\pi = 0.9 \pm 0.2\%, \\ \text{Fe}^{3+} \quad f_s &= 0.8 \pm 0.2\%, f_\sigma = 5.5 \pm 0.7\%, \\ &\quad f_\pi = 2.1 \pm 0.3\%. \end{aligned}$$

These values were derived using $f_\sigma - f_\pi = 0.35\%$ for Mn^{2+} in KMnF_3 [42] and 3.4% for Fe^{3+} in KMgF_3 [43]. Clearly, increasing the oxidation state from 2 to 3 favours σ bonding with the magnitude of f_σ increasing twice as rapidly as f_π . If parallel increases accompany the change from Cr^{3+} to Mn^{2+} we should expect $f_\sigma - f_\pi$ for Cr^{3+} to be about -0.2% at a $\text{Cr}^{3+}-\text{O}/\text{F}$ distance of about $2.4 \text{ \AA}$. An experimental value of -0.6% at $2.31 \text{ \AA}$ has been reported [43]. The estimated value of $f_\pi = 2.1\%$ in Fe^{3+} is quite close in value to the spin

If overlap effects are neglected and the normalisation constants for bonding and antibonding orbitals are assumed to be the same then the total electronic charge, C , transferred per ligand to the central cation via d orbitals in an octahedral complex is given by [44]

$$C = \left(2 - \frac{n}{2}\right)(f_\sigma + f_s) + \left(4 - \frac{2m}{3}\right)f_\pi \quad (8)$$

where n and m are the number of e_g and t_{2g} electrons respectively.

The divalent ions Mn^{2+} , Co^{2+} and Ni^{2+} in

Table 4. Spin polarisation: f_π and f'_σ for Cr^{3+} and Mn^{4+}

Ion	f_π (corrected)	f'_σ
Cr^{3+}	2.7 ± 0.6	$2.2 \pm 0.6\%$
Mn^{4+}	5.3 ± 0.8	$3.9 \pm 0.8\%$

oxide or fluoride environments show very similar charge transfers in line with the similar electron affinities. The electron affinities of Cr^{3+} , Fe^{3+} and Ni^{3+} are 31.4 eV, 30.7 eV and 35.2 eV, respectively [45]. The value of C for Ni^{3+} ($C_{\text{Ni}^{3+}}$) probably lies between 0.14 (assuming $f_\sigma = f_\pi$) and 0.15 ($f_\sigma = 2f_\pi$) [46] compared with the measured value of 0.10 for Fe^{3+} . If charge transfer follows the order of electron affinities then also bearing in mind that the apparent $C_{\text{Fe}^{3+}}$ may be reduced by spin polarisation in the $4s$ orbital [34], $C_{\text{Cr}^{3+}}$ should be somewhat larger than $C_{\text{Fe}^{3+}}$, but smaller than $C_{\text{Ni}^{3+}}$, in which case $f_\sigma + f_\pi(\text{Cr}^{3+})$ must be about 3.0 per cent. The latter quantity cannot, of course, be measured either with resonance or neutron techniques.

Acknowledgements—We wish to acknowledge many valuable discussions with Dr. A. J. Jacobson and the interest of Dr. F. A. Wedgwood in these experiments. One of us (B.C.T.) wishes to thank the Science Research Council for provision of a studentship during the course of this work and we are grateful to the S.R.C. and to A.F.R.F., Harwell for the provision of neutron facilities. We are indebted to Mr. D. H. C. Harris and members of the University Support Group at Harwell for experimental assistance.

REFERENCES

- HUBBARD J. and MARSHALL W., *Proc. Phys. Soc.* **86**, 561 (1965).
- NATHANS R., WILF G. and COX D. F., *Proc. Int. Conf. Magnetism* p. 327, Nottingham (1964).
- FENDER B. E. F., JACOBSON A. J. and WEDGWOOD F. A., *J. chem. Phys.* **48**, 990 (1968).
- JACOBSON A. J. and FENDER B. E. F., *J. chem. Phys.* **52**, 4563 (1970).
- FENDER B. E. F. and TOFIELD B. C., *NBS Spec. Publ.* No. 296, p. 51 (1968).
- SHULMAN R. G. and JACCARINO V., *Phys. Rev.* **103**, 1126 (1956).
- OWEN J. and THORNLEY J. H. M., *Rep. Prog. Phys.* **29**, 675 (1966).
- OWEN J. and STEVENS K. W. H., *Nature, Lond.* **171**, 836 (1953).
- O'REILLY D. F. and TSANG T., *J. chem. Phys.* **40**, 734 (1964).
- GALLAGHER P. K., *Mut. Res. Bull.* **3**, 225 (1968).
- GELLER S. and WOOD F. A., *Acta crystallogr.* **9**, 563 (1956).
- MORI S., HIRATA H. and IONOOKA N., *Bunseki Kagaku* **16**, 1340 (1967).
- EIBSCHUTZ M., *Acta crystallogr.* **19**, 337 (1965).
- GELLER S., *Acta crystallogr.* **10**, 243 (1957).
- WOLLAN E. O. and KOEHLER W. C., *Phys. Rev.* **100**, 545 (1955).
- MACCHESNEY J. B., WILLIAMS H. J., POTTER J. F. and SHERWOOD R. C., *Phys. Rev.* **164**, 779 (1967).
- JUDIN V. M., SHERMAN A. B. and MYL'NIKOVA I. E., *Phys. Lett.* **22**, 554 (1966).
- GODORETSKY G., SHTRIKMAN S., TENENBAUM Y. and TREVES D., *Phys. Rev.* **181**, 823 (1969).
- SHIRANE G., *Acta crystallogr.* **12**, 282 (1959).
- THE NEUTRON DIFFRACTION COMMISSION, *Acta crystallogr.* **A25**, 391 (1969).
- SWANSON H. E. and TATGE E., *NBS Circ.* **1**, 18 (1953).
- ANDERSON P. W., *Phys. Rev.* **86**, 694 (1952).
- DAVIS H. H., *Phys. Rev.* **120**, 789 (1960).
- BERTAUT E. F., BASSI G., BUISSON G., BURLET P., CHAPPERI J., DELAPALME A., MARESCHAL J., ROULT G., ALEONARD R., PAUTHENET R. and REBOUILLAT J. B., *J. appl. Phys.* **37**, 1038 (1966).
- EIBSCHUTZ M., SHTRIKMAN S. and TREVES D., *Phys. Rev.* **156**, 562 (1967).
- COPPENS P. and EIBSCHUTZ M., *Acta crystallogr.* **19**, 524 (1965).
- SMOLENSKII G. A., YUDIN V. M., SHER E. S. and STOLYPIN Yu. E., *Soviet Phys. JETP* **16**, 622 (1963).
- YUDIN V. M., GAVRIISHINA A. J., ARTSEM'YVA M. V. and BRYZHINA M. F., *Soviet Phys. solid State* **7**, 1856 (1966).
- KEESOM P. H. and PEARLMAN N., *Phys. Rev.* **91**, 1347 (1953).
- WATSON R. F. and FREEMAN A. J., *Acta crystallogr.* **14**, 27 (1961).
- OWEN J. and TAYLOR D. R., *J. appl. Phys.* **39**, 791 (1968).
- DZIALOSHINSKII I. E., *Soviet Phys. JETP* **6**, 1120, 1259 (1957).
- ALPERIN H. A., *J. phys. Soc. Japan Suppl.* **BIII**, 17, 12 (1962).
- HUBBARD J., RIMMER D. E. and HOPGOOD F. R. A., *Proc. Phys. Soc.* **88**, 13 (1966).
- NATHANS R., PICKART S. J. and ALPERIN H. A., *Bull. Am. phys. Soc.* **5**, 455 (1960); NATHANS R. and PICKART S. J., *Magnetism* (Edited by G. T. Rado and H. Suhl), Vol. 3, p. 211 (1963).
- CORLISS I. M., HASTINGS J. M., NATHANS R. and SHIRANE G., *J. appl. Phys.* **36**, 1099 (1965).
- NATHANS R., ALPERIN H. A., PICKART S. J. and BROWN P. J., *J. appl. Phys.* **34**, 1182 (1963).
- HUTCHINGS M. F. and GUGGENHEIM H. J., Unpublished.
- SHULMAN R. G. and SUGANO S., *Phys. Rev.* **130**, 506 (1963).
- BERGER S. B., BUDNICK J. I. and BURCH T. J., *Phys. Rev.* **179**, 272 (1969).
- STAUSS G. H., *Phys. Rev.* **181**, 636 (1969).
- EGASHIRA K. and HIRAKAWA K., *J. phys. Soc. Japan* **22**, 344 (1964).

43. HALL T. P. P., HAYES W., STEVENSON R. W. H. and WILKENS J., *J. chem. Phys.* **38**, 1977 (1963).
44. OWEN J., THORNLEY J. H. M. and WINDSOR C. G., *Proc. phys. Soc.* **85**, 103 (1965).
45. LOTZ W., *Institute of Plasma Phys. Rep.* No. 1/49 (1966).
46. HALL T. P. P., HAYES W., STEVENSON R. W. H. and WILKENS J., *J. chem. Phys.* **39**, 35 (1963).

A ZEROth ORDER MIXING TREATMENT OF INTERSTITIAL SOLID SOLUTIONS

KURT ALEX

Chemistry Department, William Marsh Rice University, Houston, Texas 77001, U.S.A.

and

REX B. McLELLAN

Department of Mechanical and Aerospace Engineering and Materials Science, William Marsh Rice University, Houston, Texas 77001, U.S.A.

(Received 20 January 1970)

Abstract—A comparison of zeroth and first order mixing statistics of interstitial solid solutions is presented. Conditions of applicability and limitations of the two models are discussed in relation to the solubility of carbon in austenite and of hydrogen in metals. The high temperature limit of the first order model is noted.

1. INTRODUCTION

RECENTLY a first order statistical treatment (F.O.S.) of interstitial solutions has been applied to both the equilibrium and the kinetic properties of carbon austenite[1, 2]. In this short paper a zeroth order model is considered and compared to the first order treatment. A comparison with substitutional solute also made.

this table N_u is the number of interstitial solute atoms, N_r the number of solvent atoms, β the number of interstitial sites per solvent atom, ($\beta = 1$ for octahedral sites in an fcc lattice, $\beta = 3$ for octahedral sites in a bcc lattice), and Z is the coordination number for

2. ZEROth ORDER CALCULATIONS

Consider a lattice gas of interstitials. We can distinguish the following pairs: ($u-e$), ($e-u$), ($u-u$), ($e-e$), where u represents an interstitial solute and e represents an empty interstitial site. It is helpful to construct the following table (Table 1). In

the $u-u$ pair. The energy zero is that of atoms at rest in a vacuum. In this treatment the pairs of

Table 1

Kind of pair	Number of such pairs	Energy of pairs	Total energy
$u-e$	$Z\lambda$	ϵ_u	$Z\lambda\epsilon_u$
$e-u$	$\frac{1}{2}Z(N_u-\lambda)$	ϵ_{uu}	$\frac{1}{2}Z(N_u-\lambda)\epsilon_{uu}$
$u-u$	$\frac{1}{2}Z(N_r\beta-N_u-\lambda)$	0	0
$e-e$			
Summing over all pairs	$\frac{1}{2}ZN_r\beta$		$Z\left[\lambda\epsilon_u + \frac{(N_u-\lambda)}{2}\epsilon_{uu}\right]$

a given kind do not interact with each other. Thus, the constant number of solvent-solvent pairs need not be considered in enumerating the configuration thermodynamic functions of the solution. We can write the configurational partition function in the form

$$\Omega_c = \sum_c e^{-E_c/kT}.$$

The essence of the zeroth order treatment [3] is to consider that the solute atoms are randomly distributed on their interstitial sites so that the sum over states is replaced by a single degenerate state of energy E_c . Thus,

$$\Omega_c = \frac{(N_r\beta)!}{(N_r\beta - N_u)!N_u!} \times \exp\left\{-\frac{Z}{2kT}\left[-\frac{N_u^2\Delta\epsilon}{N_r\beta} + 2N_u\epsilon_u\right]\right\},$$

since $[(N_r\beta)!/(N_r\beta - N_u)!N_u!]$ is the number of distinct configurations in the random solution and $\lambda = [N_u(N_r\beta - N_u)/(N_r\beta)]$ is the value of λ for random mixing. We obtain the configurational free energy:

$$F_c = -kT \ln \Omega_c \\ = -kT \ln \frac{(N_r\beta)!}{(N_r\beta - N_u)!N_u!} \\ + \frac{Z}{2} \left[-\frac{N_u^2\Delta\epsilon}{N_r\beta} + 2N_u\epsilon_u \right].$$

Using Stirling's theorem and differentiating with respect to N_u , we obtain the configurational chemical potential μ_u of the solute atoms,

$$\mu_u^c = kT \ln \frac{\theta/\beta}{1-\theta/\beta} - Z\Delta\epsilon \frac{\theta}{\beta} + Z\epsilon_u$$

where θ is the atom ratio N_u/N_r . Considering the infinitely dilute solution, we see that the partial energy of a solute atom at infinite dilution is,

$$\bar{E}_u^\infty = Z\epsilon_u$$

so that we can write,

$$\mu_u^c = \bar{E}_u^\infty + kT \ln \frac{\theta/\beta}{1-\theta/\beta} - Z\Delta\epsilon \frac{\theta}{\beta}. \quad (1)$$

In terms of the atom fraction C_u of solute atoms

$$\mu_u^c = \bar{E}_u^\infty + kT \ln \frac{C_u/\beta}{1 - \frac{C_u(\beta+1)}{\beta}} - \frac{Z\Delta\epsilon}{\beta} \cdot \frac{C_u}{1-C_u}.$$

It is interesting to note that the zeroth order treatment of a substitutional solution gives the result [3].

$$\mu_u^c = \bar{E}_u^\infty + kT \ln C_u + (1-C_u)^2 \omega,$$

showing a different concentration dependence of the partial energy.*

We can now compare the results for the simple zeroth order treatment with those obtained from the F.O.S. model. In this model the configurational chemical potential is,

$$\mu_u^c = \bar{E}_u^\infty - \frac{ZkT}{2} \\ \times \ln \left\{ \left[\frac{\theta/\beta}{1-\theta/\beta} \right]^2 \left(\frac{1-\theta/\beta-\phi}{\theta/\beta-\phi} \right) e^{\Delta\epsilon/kT} \right\} \\ + kT \ln \frac{\theta/\beta}{1-\theta/\beta}$$

where,

$$\phi = \frac{1 - \{1 - 4(1 - e^{\Delta\epsilon/kT}) \theta/\beta (1 - \theta/\beta)\}^{1/2}}{2(1 - e^{\Delta\epsilon/kT})}.$$

The partial configurational entropy $\bar{S}^c$ and energy $\bar{E}_u$ are:

$$\frac{\bar{S}^c}{k} = \ln \left(\frac{\theta/\beta}{1-\theta/\beta} \right)^{(Z-1)} \left(\frac{1-\theta/\beta-\phi}{\theta/\beta-\phi} \right)^{Z/2} \\ - \frac{Z\Delta\epsilon}{2kT} \cdot \frac{e^{\Delta\epsilon/kT} [\theta/\beta (1-\theta/\beta)]^2}{[2\phi (1 - e^{\Delta\epsilon/kT}) - 1]} \\ \times \frac{(1-2\theta/\beta)}{\theta/\beta (1-\theta/\beta) - \phi (1-\phi)} \quad (2)$$

* Here ω is the interchange energy [3].

and,

$$\bar{E}_u - \bar{E}_u^\infty = -\frac{Z\Delta\epsilon}{2} \left\{ 1 + \frac{e^{\Delta\epsilon/kT} [\theta/\beta(1-\theta/\beta)]^2}{2\phi(1-e^{\Delta\epsilon/kT})-1} \right. \\ \left. \times \frac{(1-2\theta/\beta)}{\theta/\beta(1-\theta/\beta)-\phi(1-\phi)} \right\}. \quad (3)$$

In the limit where $T \rightarrow \infty$ it is easy to show that equations (2) and (3) become,

$$\frac{\bar{S}_u}{k} = -\ln \frac{\theta/\beta}{1-\theta/\beta},$$

and

$$\bar{E}_u - \bar{E}_u^\infty = -Z\Delta\epsilon \theta/\beta.$$

Thus at high temperatures the F.O.S. model approaches the simple zeroth order model.

3. CONCLUSIONS

We can enumerate the following points that may be pertinent to real interstitial solid solutions.

(1) Recent data on carbon austenite[4, 5] indicates that $\bar{E}_u - \bar{E}_u^\infty$ is indeed directly proportional to θ as suggested by the zeroth order calculation. Furthermore, partial configurational entropy appears ideal. At the high temperatures and relatively low concentrations where carbon austenite is stable (900–1400°C and $\theta = 0 \rightarrow 0.07$) it is not possible to distinguish between F.O.S. and zeroth order models.

(2) The departure from zeroth order (or quasi-regular[6]) mixing should be most apparent at low temperatures when the TS -term in the free energy does not dominate E and especially if $\Delta\epsilon$ is large. In the case of hydrogen dissolved in many metals[6], the large diffusivity of H -atoms in the metal lattice has enabled equilibrium solubilities to be determined at low temperatures. In many cases, the solubility data are not compatible with either ideal or quasi-regular mixing[6]. It is suggested that these solubility data may be explained by the F.O.S. model since if the dissolved hydrogen atoms are completely ionized in solution, we may expect a large repulsive interaction between protons in nearest neighbor interstitial sites giving rise to a large value of $\Delta\epsilon$.

Acknowledgement—The authors are grateful for the support provided by the Robert A. Welch Foundation.

REFERENCES

1. McILLICAN, R. B. and DUNN, W. W., *J. Phys. Chem. Solids*, **30**, 2631 (1969).

DIRECTIONAL DISPERSION OF EXTRAORDINARY OPTICAL PHONONS IN UNIAXIAL CRYSTALS

D. J. OLECHNA

Xerox Corporation, Rochester, N.Y. 14603, U.S.A.

(Received 24 November 1969, in revised form 8 January 1970)

Abstract—A coupled harmonic oscillator formalism is used to study directional dispersion of infra-red active phonon frequencies in uniaxial crystals. Stressed is the relative ease of computation and the illumination of the degree of mode coupling. The following materials are studied: α -Quartz, CaMoO_4 , C_2WO_4 , Al_2O_3 , MgF_2 , ZnF_2 , trigonal Se, and trigonal Te.

1. INTRODUCTION

THE PRIMARY purpose of this paper is to show the ease with which a coupled harmonic oscillator method may be used to study directional dispersion of infra-red active phonon frequencies in uniaxial crystals[1]. Previous calculations by Merten[2,3] and London[4] have used a dielectric constant formalism for related studies. They calculated phonon frequencies in the extra-ordinary ray geometry as a function of the angle between the optic axis and the direction of propagation. The interpolation scheme here is based on a phenomenological treatment[1,5] which makes use of the free phonons, in the absence of anharmonicity, are independent of each other and have properties of harmonic oscillators. The advantages include: providing a simple procedure for obtaining the matrix from which eigenvalues and eigenvectors of the normal modes are obtained, focusing clearly on the coupling mechanism that generates the new normal modes, and being sufficiently general so that it is easily extended to treat the directional dispersion of other elementary excitations in anisotropic media.

In Section 2 the phenomenological model is developed and the numerical procedure described. The results of the calculations on several representative materials are presented in Section 3 along with the input parameters used to compute them. The reader who is

interested in greater detail on any specific material may readily reproduce the results.

2. PHENOMENOLOGICAL MODEL

The derivation of this technique starts, as it does in the dielectric constant formalism [2-4], with the equations of motion. Perpendicular to the c -axis, the equation of motion for the i th mode is

$$m_i \ddot{u}_i(t) + m_i \omega_i^2 u_i(t) = e^*(i) E_c^p(t) \quad (1)$$

are referred to as $u_+(j)$ and $u_-(j)$ respectively. Let θ be the angle between c -axis and the incident E field. The macroscopic polarization in Z direction couples the orthogonal modes for $0^\circ < \theta < 90^\circ$ and is given by

$$P_Z^p = u_+(j) e_A^*(j) \sin \theta - u_-(j) e_c^*(j) \cos \theta. \quad (2)$$

In the E and A directions

$$P_E^p = -P_Z^p \cos \theta \quad \text{and} \quad P_A^p = P_Z^p \sin \theta. \quad (3)$$

Since $E_{\text{eff}} = -4\pi P$, substituting equations (3) into equations (1) and the equivalent for the parallel direction yields

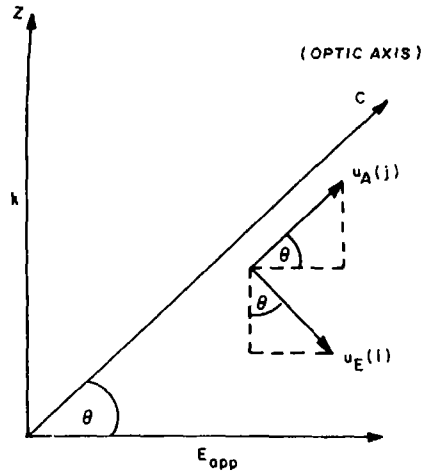


Fig. 1 Geometrical configuration used throughout this paper.

$$\begin{aligned} & [m\omega_k^2(i) + 4\pi(e_k^*(i))^2 \cos^2 \theta - m\omega^2]u_k(i) \\ & + 4\pi e_k^*(i) \sum_{j \neq i} e_k^*(j) \cos^2 \theta u_k(j) \\ & - 4\pi e_k^*(i) \sum_j u_j(i) e_j^*(j) \sin \theta \cos \theta = 0 \quad (4) \end{aligned}$$

and

$$\begin{aligned} & [m\omega_l^2(i) + 4\pi(e_l^*(i))^2 \sin^2 \theta - m\omega^2]u_l(i) \\ & + 4\pi e_l^*(i) \sum_{j \neq i} e_l^*(j) \sin^2 \theta u_l(j) \\ & - 4\pi e_l^*(i) \sum_j u_k(i) e_k^*(i) \sin \theta \cos \theta = 0. \quad (5) \end{aligned}$$

The desired mode frequencies are then determined from the secular equation, (see page 2757) where $\Omega_k(i)$ and $\Omega_l(i)$ are the mode plasma frequencies, and $\omega_k^l(i)$ and $\omega_l^l(i)$ are the longitudinal phonon frequencies in the absence of coupling. These are related by

$$\Omega_k(i) = [(\omega_k^l(i))^2 - \omega_k^2(i)]^{1/2}. \quad (7)$$

The experimental $L0$ and $T0$ phonon frequencies determine the input parameters. The $\omega_k(i)$ and $\omega_l(i)$ values are $T0$ frequencies as

measured at $\theta = 90^\circ$ and 0° , respectively. The $\omega_k^l(i)$ and $\omega_l^l(i)$ are not the measured $L0$ phonon frequencies, due to the coupling of the $L0$ modes by the macroscopic field at both 0 and 90° . The values of $\omega_k^l(i)$ and $\omega_l^l(i)$ are obtained, via an iterative process, by matching the eigenvalues of the reduced secular equation with the experimental results at $\theta = 0$ and 90° . The iteration process involves taking the previous guess at $\omega_k^l(i)$ or $\omega_l^l(i)$ adding to it the experimentally determined ω and subtracting the previously obtained eigenfrequency.

Experimental longitudinal frequencies are usually good choices for initial guesses. It should be noted that $\omega_k^l(i)$ or $\omega_l^l(i)$ must be greater than or equal to the corresponding $\omega_k(i)$ or $\omega_l(i)$. Convergence is usually very rapid. In fact, the entire directional dispersion results for α -quartz (including iteration to obtain uncoupled values of the $L0$ phonon frequencies, eigenvalues and vectors for the 12 modes with θ varying from 0 to 90° in steps of 15°) were obtained in less than 8 sec on the Univac 1108 computer.

In the trivial case of two coupled harmonic oscillators this formalism is identical to the dielectric constant approach of Merten[2] and the measured $L0$ phonon frequencies are identical to $\omega_k^l(i)$ and $\omega_l^l(i)$. Due to the iterative step required in the oscillator formalism, an analytical comparison for systems requiring more than two oscillators is impossible. However all of the eigenvalues resulting from our calculation for α -quartz agreed with those of Merten[2] to within 1 or 2 digits in the fourth significant figure.

3. NUMERICAL CALCULATIONS

It is now a simple matter to determine the eigenvalues and vectors for a number of representative uniaxial crystals. The degree to which one mode couples with another is indicated by the square of the components of the mode eigenvectors. The essential input frequencies that were used in the final com-

$$\begin{array}{c}
 \omega_{2^{-1}}(1) + \Omega_{2^{-1}}(1) \cos^2 \theta - \omega^2 \\
 \vdots \\
 \Omega_{2^{-1}}(N) \Omega_{2^{-1}}(1) \cos^2 \theta \\
 \vdots \\
 -\Omega_{2^{-1}}(1) \Omega_{2^{-1}}(1) \sin \theta \cos \theta \\
 \vdots \\
 -\Omega_{2^{-1}}(1) \Omega_{2^{-1}}(M) \sin \theta \cos \theta
 \end{array}
 \begin{array}{c}
 \Omega_{2^{-1}}(1) \Omega_{2^{-1}}(2) \cos^2 \theta \\
 \vdots \\
 \omega_{2^{-1}}(N) - \Omega_{2^{-1}}(N) \cos^2 \theta \\
 \vdots \\
 -\Omega_{2^{-1}}(N) \Omega_{2^{-1}}(1) \sin \theta \\
 \vdots \\
 \omega_{2^{-1}}(M) - \Omega_{2^{-1}}(M) \sin^2 \theta - \omega^2
 \end{array}
 \begin{array}{c}
 \cos \theta \\
 \sin \theta \cos \theta \\
 \vdots \\
 \theta - \omega^2 \\
 \vdots \\
 \cdot
 \end{array}
 \begin{array}{c}
 -\Omega_{2^{-1}}(1) \Omega_{2^{-1}}(1) \sin \theta \cos \theta \dots - \Omega_{2^{-1}}(1) \Omega_{2^{-1}}(M) \sin \theta \cos \theta \\
 \vdots \\
 -\Omega_{2^{-1}}(N) \Omega_{2^{-1}}(M) \sin \theta \cos \theta \\
 \vdots \\
 \Omega_{2^{-1}}(1) \Omega_{2^{-1}}(2) \sin^2 \theta \dots \cdot \\
 \vdots \\
 \omega_{2^{-1}}(M) - \Omega_{2^{-1}}(M) \sin^2 \theta - \omega^2
 \end{array}
 \begin{array}{c}
 u_2(1) \\
 \vdots \\
 u_2(N) \\
 \vdots \\
 u_2(1) \\
 \vdots \\
 u_2(M)
 \end{array}
 \begin{array}{c}
 = 0 \\
 (6)
 \end{array}$$

puter program are presented in Table 1. The references for the experimental $L0$ and $T0$ frequencies from which the calculations initiated are as follows: α -quartz[2, 3], CaMoO_4 and CaWO_4 [6], Al_2O_3 [7], MgF_2 and ZnF_2 [8], trigonal Se and Te[9, 10]. For each material we have plotted frequencies as a function of the angle between the c -axis and the crystal surface. For identification the modes are numbered in order of increasing frequency. The character of each mode is designated by the letters l and t , standing for longitudinal and transverse, respectively.

The simplest uniaxial crystals studied were trigonal Se and Te (see Fig. 2). These were the only cases where the iteration step was not necessary. Each of these crystals has three infra-red active modes, two E modes where the mode vibrations are perpendicular to the c -axis and one A_2 mode where the vibrations are parallel to the c -axis. In each case one of the E modes is weak (small $L0$ - $T0$ phonon frequency splitting) and occurs at frequencies

well removed from the other modes. Hence, this mode does not strongly influence the coupling between the other two modes. For Se, the directional dispersion in the two low frequency modes is an illustration of large anisotropic splitting. The corresponding modes in Te illustrate conversely the case of small anisotropic splitting[1]. The strongest coupling between the modes, labeled 1 and 2, occurred in Te at $\theta = 60^\circ$ (this coupling was 42 per cent). For Se this coupling did not exceed 0.3 per cent at any angle.

Alpha-quartz has been extensively studied in the literature[2, 3, 5, 11, 12] and is also included in this report. The calculated directional dispersion results for extraordinary phonons are shown in Fig. 3. Note that our angle convention differs by $(90^\circ - \theta^\circ)$ from that used by Merten[2, 3]. Alpha-quartz has eight E modes and four A_2 modes (eight of the branches have either $l \rightarrow t$ or $t \rightarrow l$ character, two have $t \rightarrow t$ character, and two $l \rightarrow l$ character). To illustrate mode coupling

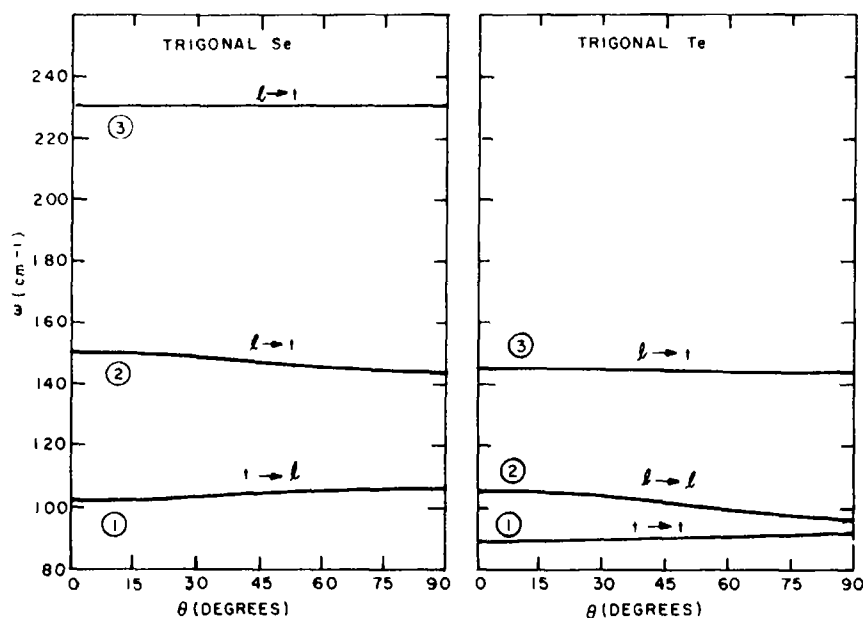


Fig. 2. Directional dispersion curves for trigonal Se and Te.

in this more complicated system, selected eigenvectors for α -quartz at $\theta = 75^\circ$ are presented in Table 2. Note that proximity of the levels is not the sole determining factor in the extent to which the modes couple.

Several other materials were studied by this procedure. Directional dispersion results for CaMoO_4 and $\text{CaWO}__4$ are presented in

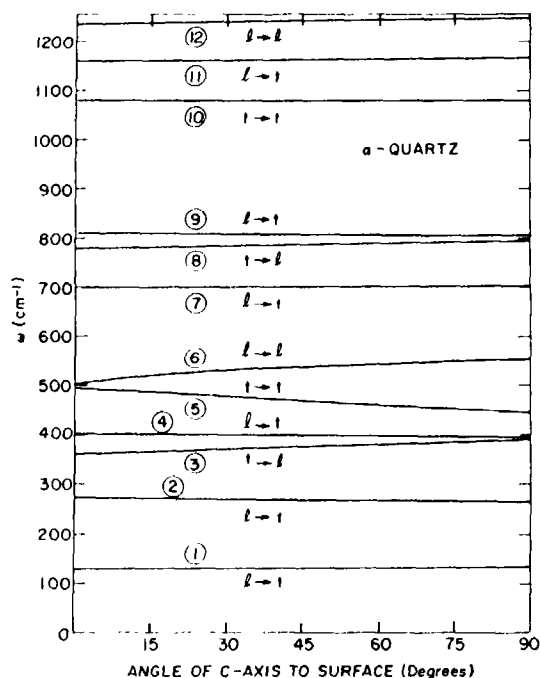


Fig. 3. Direction dispersion curves for α -quartz.

Fig. 4 and those for MgF_2 and ZnF_2 in Fig. 5. In the former cases there exists two $l \rightarrow l$ modes, two $t \rightarrow t$ modes, two $l \rightarrow t$ modes and two $t \rightarrow l$ modes. In the latter cases each have one mode of $l \rightarrow l$ character, one of $t \rightarrow t$ character, and two modes of $l \rightarrow t$ character. Despite the proximity of many of the modes to one another no difficulty arose in obtaining solutions in any of these cases. It was only for corundum ($\alpha\text{-Al}_2\text{O}_3$) that a minor problem occurred. This came about because very strong coupling exists in $\alpha\text{-Al}_2\text{O}_3$ at $\theta = 0^\circ$ between three modes, those labeled (3), (5) and (6) in

Table 2. Selected eigenvectors for α -quartz at $\theta = 75^\circ$

Frequency (cm^{-1})	384.4	396.3	788.0	798.9
Mode no.	3	4	8	9
1	-0.003	0.002	-0.001	0.000
2	-0.019	0.010	-0.004	0.002
3	0.903	-0.345	0.034	-0.023
4	0.371	0.927	-0.008	0.005
5	0.092	-0.069	-0.016	0.010
6	-0.189	0.130	0.065	-0.040
7	0.004	-0.002	-0.012	0.007
8	-0.024	0.015	0.944	-0.294
9	0.007	-0.004	0.303	0.952
10	0.011	-0.007	0.028	-0.019
11	0.000	0.000	0.000	0.000
12	-0.040	0.025	-0.098	0.066

Fig. 6. The strong coupling between three modes means that the $L0$ frequencies are not good starting guesses for input as uncoupled $L0$ phonon frequencies. In this case the approach to a solution in the iterative step

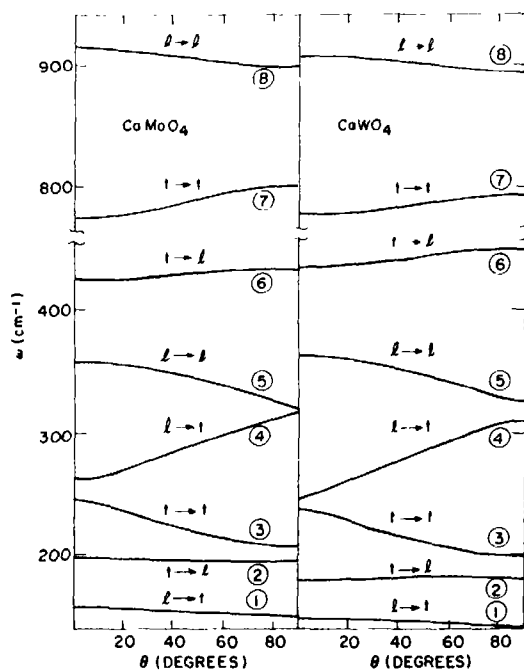
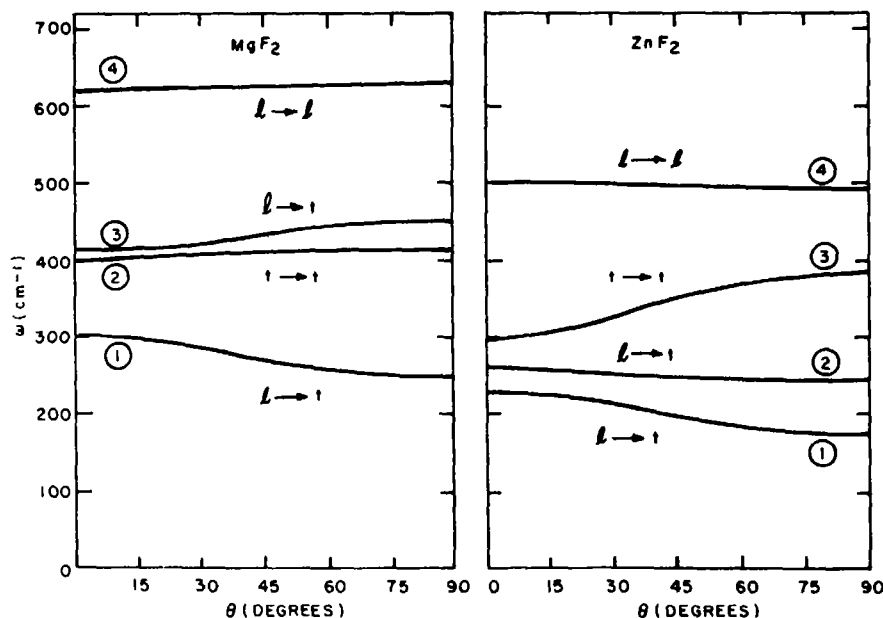
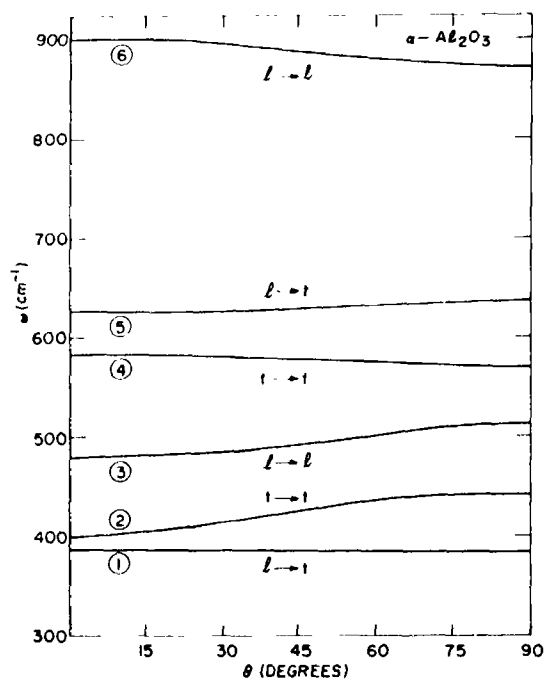


Fig. 4. Direction dispersion curves for CaMoO_4 and CaWO_4 .

Table 3. Eigenvectors for $\alpha\text{-Al}_2\text{O}_3$ at $\theta = 0^\circ, 45^\circ, 90^\circ$. (Columnwise, corresponding to increasing order of eigenvalues)

(deg)		0						45						90					
Frequency		387	400	480	583			426	491	578	629	887		385	442	512	569	635	871
Mode no.		1	2	3	4				3	4	5	6		1	2	3	4	5	6
1		0.987	0	0.105	0	-		84	0.086	0.007	-0.014	0.086		1.000	0	0	0	0	0
2		0	1.000	0	0	-		92	-0.525	-0.038	0.076	-0.466		0	1.000	0	0	0	0
3		-0.149	0	0.876	0	-		107	0.622	0.032	-0.060	0.329		0	0	0.722	0	0	0.692
4		0	0	0	1.000	-		98	0.311	0.785	0.235	-0.476		0	0	0	1.000	0	0
5		-0.017	0	-0.113	0	-		128	-0.110	-0.040	0.939	0.312		0	0	0	0	1.000	0
6		-0.054	0	-0.456	0	-		96	-0.469	0.617	-0.230	0.580		0	0	-0.692	0	0	0.722

Fig. 5 Directional dispersion curves for MgF_2 and ZnF_2 .Fig. 6. Directional dispersion curves for $\alpha\text{-Al}_2\text{O}_3$.

which determines the $L0$ phonon frequencies is highly non-linear. Hence several trial values for them had to be tested in order to find one set of frequencies that was close enough to actuality to permit convergence. The extent of the mode coupling for $\alpha\text{-Al}_2\text{O}_3$ is shown in Table 3 where the eigenvectors are presented for $\theta = 0, 45$ and 90° .

The coupled harmonic oscillator formalism, while not formally as elegant as the dielectric constant approach used by Merten[2, 3] and London[4], provides a simple and efficient method for calculating the directional dispersion and determining the degree of mode coupling. While we have only considered uniaxial crystals in this study, extension of the method to biaxial crystals may be readily accomplished for propagation directions lying in planes determined by the principle crystal axes.

Acknowledgement—The author is indebted to G. Lucovsky, who suggested this problem, for many stimulating discussions.

REFERENCES

1. LUCOVSKY G., BURSTEIN E. and PINCZUK A., *Bull. Am. phys. Soc.* **14**, 740 (1969).
2. MERTEN L., *Phys. Status Solidi* **28**, 111 (1968).
3. MERTEN L., *Z. Naturf.* **23a**, 1183 (1968).
4. LOUDON R., *Adv. Phys.* **13**, 423 (1964).
5. ONSTOTT J. and LUCOVSKY G., *Bull. Am. phys. Soc.* **14**, 740 (1969).
6. BARKER A. S., Jr., *Phys. Rev.* **135**, A742 (1964).
7. BARKER A. S., Jr., *Phys. Rev.* **132**, 1474 (1963).
8. BARKER A. S., Jr., *Phys. Rev.* **136**, A1290 (1964).
9. LUCOVSKY G., KEEZER R. C. and BURSTEIN E., *Solid St. Commun.* **5**, 439 (1967).
10. In a private communication, G. Lucovsky indicated that the constant frequency of the highest *E*-type mode in Se should be 230 cm^{-1} rather than the value 225 cm^{-1} which given in the preceding reference. The data is considered accurate to within one wave number.
11. SCOTT J. F. and PORTO S. P. S., *Phys. Rev.* **161**, 903 (1967).
12. SPITZER W. G. and KLEINMAN D. A., *Phys. Rev.* **121**, 1324 (1961).

PERTURBATION OF FUNDAMENTAL BAND EDGE ABSORPTION OF NaClO_3 CRYSTALS AT HIGH TEMPERATURES

S. B. S. SASTRY, R. B. TRIPATHI and C. RAMASASTRY

Solid State Physics Laboratory, Physics Department, Indian Institute of Technology,
Madras 36, India

(Received 30 December 1969)

Abstract—The fundamental absorption band edge of NaClO_3 crystal showed a shift towards longer wavelengths with increase in temperature. There is also evidence of formation of a new band at temperature higher than about 120°C . The shift is nearly linear up to about 120°C , but it is much larger than the linear rate as the melting point ($\approx 250^\circ\text{C}$) is approached. The excess absorption is assumed to be due to the thermally produced lattice disorder and analysis yielded 1.40 ± 0.05 eV for the energy of formation of the defect. The anomalous thermal expansion of the crystal reported by earlier workers at temperatures above 120°C could also be analysed in a similar manner and the activation energy of 1.45 ± 0.05 eV so obtained is in reasonable agreement with that obtained from optical absorption studies. The additional absorption may be attributed to the perturbation of the fundamental absorption band due to defects formed at higher temperatures.

1. INTRODUCTION

IT IS KNOWN that ionic crystals like alkali halides and silver halides absorb strongly in the ultraviolet[1-3]. It is referred to as the fundamental absorption of the crystal, generally assumed to be due to the transition of the electron of the anion to a neighbouring cation. However, attempts to calculate the energy of the transition on this model are entirely unsuccessful. The long wavelength tail of this strong absorption has been of considerable interest as regards shape, fine structure, effect of crystal imperfections and its dependence on temperature. Point defects like impurity atoms, vacancies and interstitials should perturb these transitions. The α , β and γ [4, 5] bands in alkali halides with colour centres are ascribed to such transitions occurring near point defects. In a similar way thermally produced point defects also should perturb the edge. The exciton absorption is also revealed in the long wavelength tail of the fundamental absorption especially in spectra taken under high resolution at low temperatures[6, 7].

In our efforts to produce and explain Colour Centres in sodium chlorate crystal[8] a band

similar to the β -band in alkali halides was observed around 228 nm (5.44 eV) in the long wavelength edge of the fundamental band. This band is due to the absorption of the

2. EXPERIMENTAL

Thin clear crystals of about $1 \times 0.5 \times 0.05$ cm³ were used for absorption measurements. A special mount housed the crystal with heating coils on either side. A thermocouple fixed very near the crystal in the mount measured the temperatures. The supply to the heating coils was from a constant voltage source and about 15 min was allowed for the crystal to attain constant temperature for each change of the heater current. The temperature is constant to within $\pm 2^\circ$ during each measurement. Absorption measurements were made on a

Zeiss PMQ II spectrophotometer. The special mount was held in a separate stand between the exit slit of the monochromator and the detector assembly. In all subsequent measurements the position of the crystal was not disturbed in any way and the light intensity transmitted by the crystal at each wavelength was measured at different temperatures for the same setting of the slit width and the gain of the measuring unit. Agreement between the readings taken at any particular temperature during raising and lowering of temperature within 0.01 on the optical density scale amply confirmed that the hydrogen lamp and the measuring unit of the spectrophotometer were sufficiently stable and that the crystal does not have any appreciable thermal hysteresis. Data at photon energies higher than about 5.7 eV are not fully reliable because of stray light problem of the spectrophotometer in the extreme ultraviolet and the relative insensitivity of the instrument at the higher optical densities. It must be mentioned that all the changes produced in the spectra on heating the crystal are completely reversible.

3. RESULTS AND DISCUSSION

The absorption spectra of a thin (0.45 mm) crystal of Sodium Chlorate at different temperatures are shown in Fig. 1. They represent the long wavelength edge of the so called fundamental absorption of the crystal, the absorption maximum lying at energies higher than 6 eV [8]. The strong fundamental absorption of KClO_3 crystals also lies in this region but slightly shifted to higher energies [9].

The effect of increase in temperature of the crystal results in the shifting of the long wavelength edge to longer wavelengths. At each photon energy the absorption constant of the crystal increases with temperature and the photon energy corresponding to any particular absorption constant shifts to smaller energies. Following Dash and Newman [10] these may be referred to as vertical and horizontal shifts. Further at higher temperatures, the absorption curves show a hump which becomes more

prominent as the melting point of the crystal ($\approx 250^\circ\text{C}$) is approached.

An earlier study [11] has shown that the shape of the absorption curves obey the Urbach relation [12]

$$K = K_0 e^{-B(h\nu_0 - h\nu)/kT} \quad (1)$$

where K is the absorption constant at energy $h\nu$, and K_0 and $h\nu_0$ are the maximum absorption constant and the energy at which this occurs respectively. B is a constant, T is the temperature in absolute scale and k is the Boltzmann constant. The fit was reasonably good up to absorption constant of 100 cm^{-1} but the departures from this rule are particularly prominent in the higher temperature curves. This led us to examine if a new band is developing at these high temperatures.

The shift of the photon energy for each absorption constant is shown in Fig. 2 (continuous lines). It is linear up to about 120°C , but at higher temperatures there are prominent deviations from linearity. This is taken to be an indication of the presence of additional absorption at these temperatures. If one follows the method of Dash and Newman [10] and tries to coincide the curves by suitable combination of horizontal and vertical shifts it is again found that the superposition of the curves is possible only for temperatures below 120°C . There are large departures at high temperatures, which of course is to be expected because of the differences in the shapes of the curves for the higher and lower temperatures.

It may be noted that Dash and Newman [10] could successfully superpose the absorption curves of silicon and germanium taken at 77 and 300°K which are far lower than the melting points of these crystals. It is however very interesting that such a superposition is at all possible for the ionic crystals NaClO_3 . The reason for this is at present not known except that in the case of silicon or germanium the long wavelength shift was attributed to a decrease of band gap and the vertical shift to

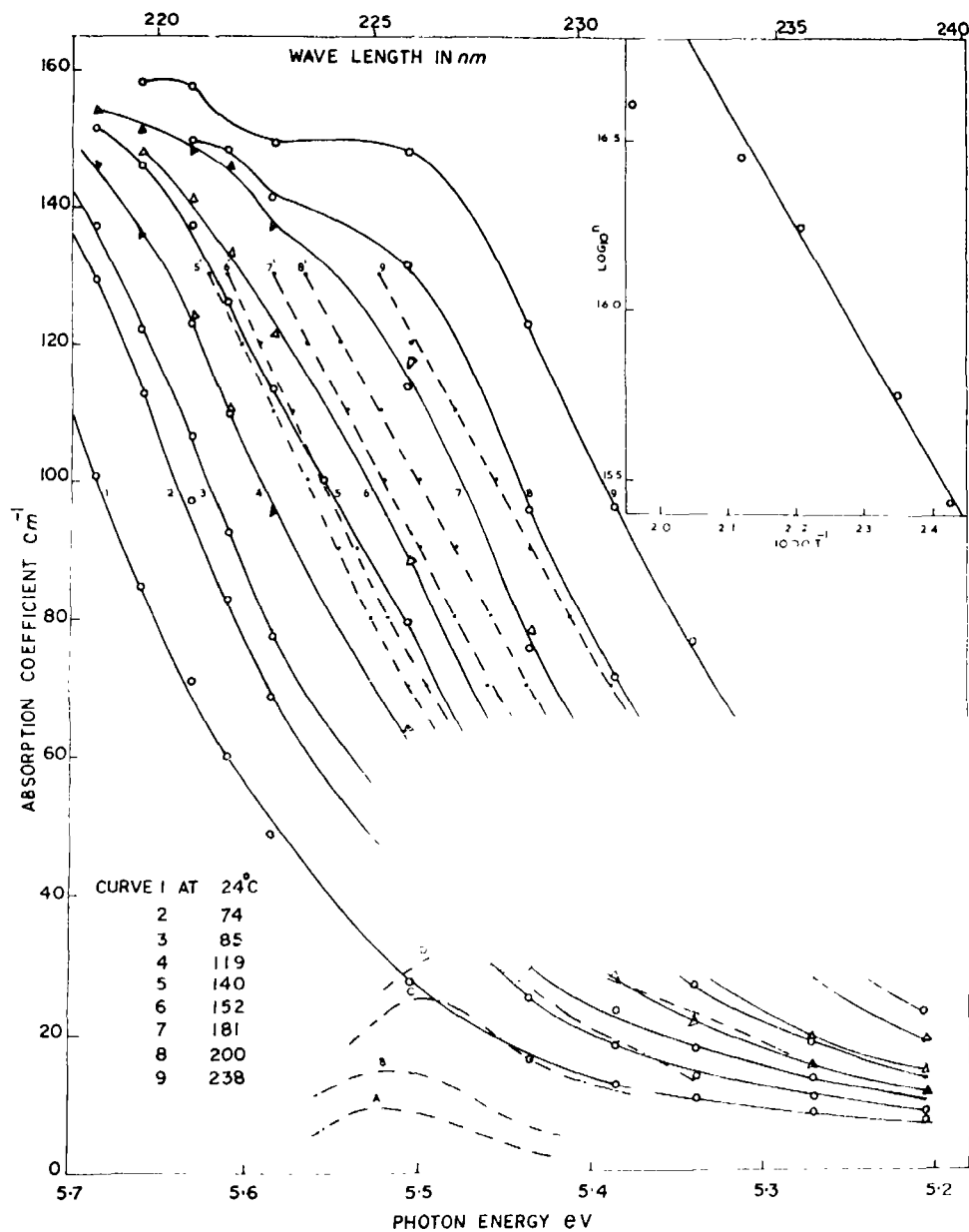


Fig. 1. Absorption spectra of NaClO₃ crystal (0.45 mm thick) at different temperatures between 25 and 240°C. The circles indicate data taken while heating Δ indicates those taken while cooling the crystal. Inset log₁₀ n vs. T^{-1} plot.

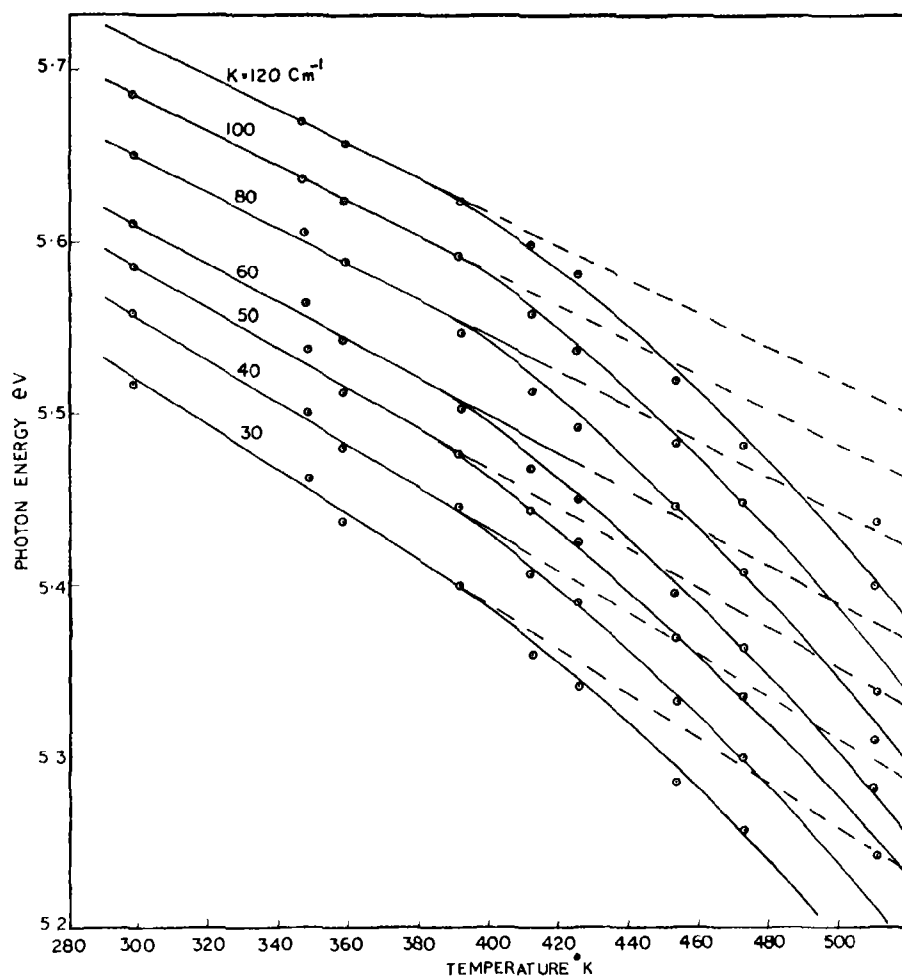


Fig. 2 Photon energy vs. temperature plots for various absorption constant values (For clarity only 7 lines are shown)

altered phonon interaction. If the same explanation is to be used here also, one has to possibly invoke, the idea that the ionic crystals could be looked upon as large band gap semiconductors. It is however difficult at this stage to attribute unequivocally the observed horizontal shift (shift to long wavelengths) to a decrease in the band gap of NaClO_3 crystal.

Quite empirically, it is possible to extrapolate the linear parts of Fig. 2 (dashed lines) and

predict the absorption curve at any higher temperature. This would correspond to the case of regular shift to long wavelengths provided there is no new absorption band. The curves so predicted are shown by dashed lines in Fig. 1 for temperatures 140, 152, 181, 200 and 238°C (curves 5'-9'). The experimentally observed absorption in excess of these predicted curves is shown in the same figure (curves A, B, C, D and E). It represents a new band

increasing in intensity with temperature. The number of absorption centres responsible for this band is computed at each temperature using the Smakula-Dexter formula[13]

$$nf = 0.87 \times C \times K \times W \times 10^{17} \quad (2)$$

where n is the number of centres, f is the oscillator strength, C is a factor dependant on refractive index μ and is given by $\mu/(\mu^2 + 2)^2$, K is the absorption constant at the peak of the band in cm^{-1} and W is the width of the band at half maximum in electron volts. In this calculation the half width chosen for the band is twice the difference between the peak position and the energy at which the absorption falls to 0.5 of the peak height on the long wavelength side of the band. For reasons already mentioned the short wavelength side of the band is not fully reliable. A value of 1.9 was used for the oscillator strength f , which is the estimated value for the α -band (perturbation due to a vacancy) in alkali halides by Dexter[14]. The value used for estimating C in the formula (2) is 1.51 and its variation with temperature, though very small is taken into account. Concentrations obtained are $2.7, 5.7, 10$ and $40 \times 10^{15}/\text{cc}$ at temperatures 140, 170, 200 and 238°C respectively. A similar calculation using the simpler formula for nf [15]

$$nf = 1.131 \times K \times W \times 10^{12}$$

with the same notation as in equation (2), excepting that W is to be substituted in wave-numbers, also gave for n , values of the same order namely 3.4, 7.2, 21.6, 34.5 and $50.4 \times 10^{15}/\text{cc}$ respectively for the temperatures mentioned above. These concentrations when plotted against inverse of temperature T^{-1} on a semi log paper (inset, Fig. 1) gave a straight line representing an activation energy of 1.40 ± 0.05 eV.

As the new band is making its appearance only at high temperatures it is reasonable to assume that it is a consequence of thermal disorder in the crystal. Preliminary measure-

ments on electrical conductivity of the crystal in this laboratory showed that the intrinsic region of electrical conduction is above 120°C for this crystal and the energy for defect formation is about 1.8 eV. Hence it may be reasonable to associate the increased optical absorption at elevated temperatures with thermal defects.

This interpretation can be supported from another angle. The thermal expansion data of NaClO_3 crystals obtained by Sharma[16] by an accurate interferometric method showed an anomalous behaviour at higher temperatures. The data of Sharma is shown in Fig. 3 which displays a considerable departure from linear rate for temperature above 120°C . According to Lidiard[17] such an anomalous expansion is expected for ionic crystals in the intrinsic range of temperatures. The idea has been well utilised by Merriam *et al.*[18] in the case of NaCl and by Nicklow and Young[19] in the case of silver halides to calculate the energies of formation of defects, which are in reasonable agreement with those obtained by other methods. The presence of defects produce a

$$\Delta\alpha = \frac{1}{V} \frac{d(\Delta V)}{dT} = \frac{AE}{2kT^2} e^{-E/2kT}$$

so that

$$T^2(\Delta\alpha) = A' e^{-E/2kT} \quad (4)$$

The experimental values of α are taken from the Fig. (3) and $T^2(\Delta\alpha)$ vs. T^{-1} plot on a semi-log paper (Fig. 4) has given a straight line the slope of which corresponds to an activation energy of 1.45 ± 0.05 eV. This is in reasonable agreement with the value $(1.40 \pm 0.05$ eV) obtained from an analysis of the temperature

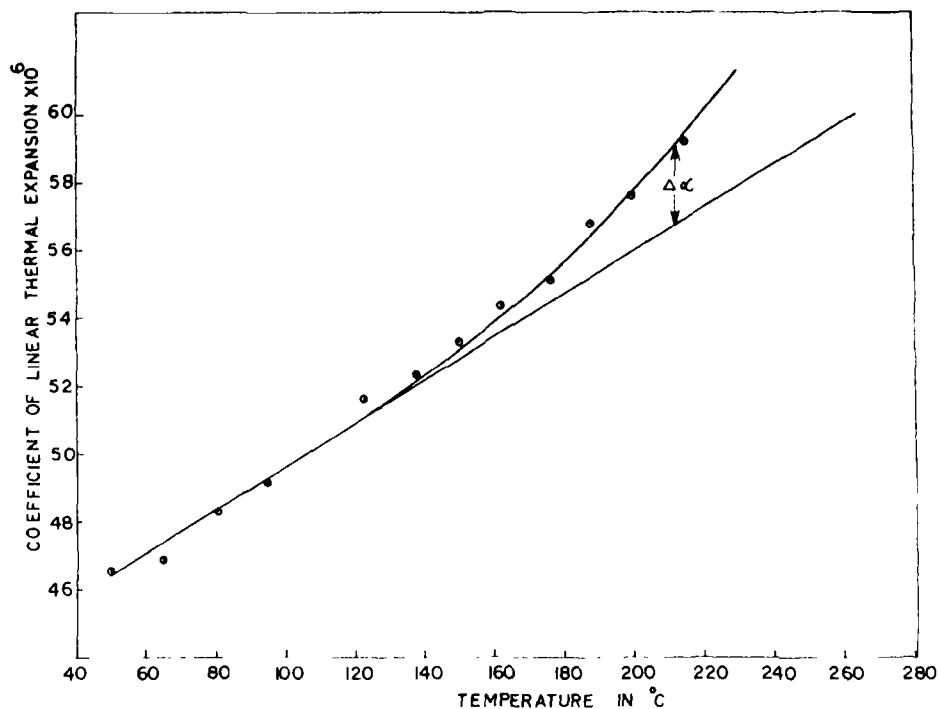


Fig. 3 Variation of thermal expansion of NaClO_4 crystal with temperature (plotted with data of Sharma[16])

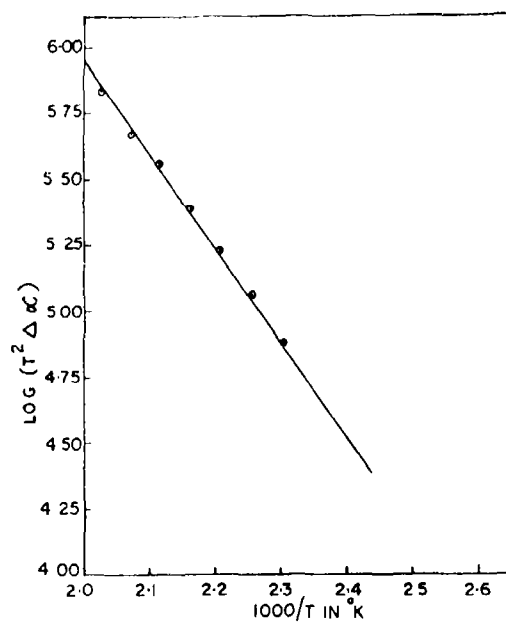


Fig. 4. $\log_{10}(T^2 \cdot \Delta\alpha)$ vs. T^{-1} plot.

dependance of optical absorption presented in the earlier part of this paper.

We are thus led to attribute both the anomalous thermal expansion and the excess optical absorption of NaClO_3 crystals to thermally produced defects. Whether these defects are of the Frenkel type or the Schottky type is yet to be decided. The new band representing the excess optical absorption may be thought of as a perturbation of the long wavelength edge of the fundamental absorption by the thermal defects.

REFERENCES

1. HILSCH R and POHL R W, *Z. Phys.* **59**, 812 (1930).
2. FESEFELDT H, *ibid* **64**, 623 (1930), *ibid* **64**, 741 (1930).
3. SCHNEIDER F. G. and O'BRYAN H. M., *Phys. Rev.* **51**, 293 (1937).
4. DEBELQ C. J., PRINGSHEIM P. and YUSTER P. J., *J. Chem. Phys.* **19**, 574 (1951) *ibid* **20**, 746 (1952).
5. KILICK C. C. and PATTERSON D. A., *Phys. Rev.* **130**, 2169 (1963).
6. MARTIENSSEN W., *J. Phys. Chem. Solids* **8**, 294 (1959).
7. JOESTEN B. L. and BROWN F. C., *Phys. Rev.* **148**, 919 (1966).
8. RAMASASTRY C. and SASTRY S. B. S., *J. phys. Soc. Japan* **18**, 1220 (1963) *Ind. J. pure and appl. Phys.* **3**, 414 (1965).
9. RAMASASTRY C. and SASTRY S. B. S., *J. phys. Chem. Solids* **29**, 399 (1968).
10. DASH W. C. and NEWMAN R., *Phys. Rev.* **99**, 1159 (1955).
11. RAMASASTRY C., SASTRY S. B. S. and RAMESH MURTHY R., *Proc. Nucl. Phys. and Solid State Phys. Symposium, Madras, India*, p. 340 (1968).
12. URBACH F., *Phys. Rev.* **92**, 1324 (1953).
13. COMPTON W. D. and RABIN H., *Solid State Physics* (Edited by F. Seitz and D. Turnbull), Vol. 16, p. 154, Academic Press, New York (1964).
14. DEXTER D. L., *Phys. Rev.* **83**, 1044 (1951).
15. MOTT N. F. and GURNEY R. W., *Electronic Processes in Ionic Crystals*, p. 103, Clarendon Press, London (1957).
16. SHARMA S. S., *Proc. Ind. Acad. Sci.* **31A**, 83 (1950).
17. LIDIARD A. B., *Handbuch der Physik*, (Edited by S. Flugge) Vol. 20, p. 260, Springer, Berlin (1957).
18. MERRIAM H. F., SMOLUCHOWSKI R. and WIEGAND D. A., *Phys. Rev.* **125**, 65 (1962).
19. NICKLOW R. M. and YOUNG R. A., *Phys. Rev.* **129**, 1936 (1963).

CONDUCTION A DEUX BANDES ET EFFET DE PERIODE DANS LES ALLIAGES A BASE DE NICKEL ET DE COBALT

J. DURAND et F. GAUTIER

Equipe de Recherches sur la Structure Electronique des Solides, Associee au CNRS n° 100.
Institut de Physique, 3, rue de l'Université, 67 Strasbourg, France

(Received 7 October 1969)

Résumé—Des mesures de résistivité électrique à 4°K, 77 et 297°K sur des alliages dilués de nickel avec les deuxième et troisième séries de transition et sur des alliages dilués de cobalt avec les éléments des trois séries de transition ont permis de montrer l'existence dans ces alliages d'états liés virtuels, l'existence d'un effet de période et la validité d'un modèle de conduction à deux bandes.

En analysant les déviations à la loi de Matthiessen en fonction de la concentration en impuretés, on a pu séparer les contributions des bandes $s\uparrow$ et $s\downarrow$ à la résistivité pour le nickel, le cobalt et les éléments de transition dans le nickel et le cobalt. De plus, on a mis en évidence l'existence d'un terme de mélange de spin qui, au moins pour les alliages de nickel à 77°K, est du même ordre de grandeur que les résistivités associées à chaque bande de la matrice.

Une telle séparation est indispensable pour faire apparaître sans ambiguïté les états liés virtuels et pour rendre manifeste l'effet de période dont on propose une explication qualitative.

Abstract—Electrical resistivities of dilute alloys of nickel with 4d and 5d transition elements and of cobalt with other transition metals have been measured at 4, 77 and 297 K. The results point out the existence of virtual bound states in some of these alloys, the existence of a period effect and the validity of two bands conduction model.

By analyzing the impurity concentration dependence of the deviations from Matthiessen's rule, the resistivities in both $s\uparrow$ and $s\downarrow$ bands have been derived for nickel, cobalt and for the transition elements in nickel and cobalt. This study has shown the existence of a spin mixing term, at least in the nickel alloys at 77°K, of the same order of magnitude as the resistivities associated with each band of the matrix. A qualitative explanation for the period effect is proposed.

INTRODUCTION

DANS une note antérieure[1], nous avons montré que les mesures de résistivité électrique sur les alliages NiRh, NiRu, NiTi, NiRe s'accordent avec les mesures d'aimantation, de diffraction de neutrons et de RMN pour attester la présence d'un état lié virtuel au niveau de Fermi. Cet état est extrait de la bande pleine du nickel, selon le schéma proposé par Friedel[2], pour une différence de charge $|Z|$ plus faible que dans le cas des alliages de nickel avec la première série de transition.

Nous présentons ici les résultats de mesures de résistivité électrique à 4, 77 et 297°K sur les alliages de nickel avec les deuxième et troisième séries de transition et sur les alliages de cobalt avec les éléments des trois séries de métaux de transition.

ment de spin dues aux impuretés ou aux phonons: les bandes $s\uparrow$ et $s\downarrow$ ont des conductibilités différentes puisque les bandes d_{σ} ($\sigma = \uparrow, \downarrow$) auxquelles elles sont couplées ne sont pas identiques.

La validité de ce modèle a été démontrée sans ambiguïté par les études récentes sur les alliages à base de métaux de transition ferromagnétiques. Campbell *et al.*, Farrell et Greig, Schwerer *et al.* ont mis en évidence de fortes déviations à la loi de Matthiessen dans les alliages à base de nickel et de fer entre 4-40°K[4]. Ces déviations peuvent être attribuées à une conduction à deux bandes

pourvu que ces bandes soient couplées entre elles par des transitions avec renversement de spin. Le terme de mélange de spin $\rho \uparrow \downarrow$ ainsi introduit correspond à des transitions dues aux interactions électron-électron[5] et électron-magnon[6]; il varie, dans le cas du nickel, proportionnellement à T^2 et est du même ordre que les résistivités associées à chaque bande s_σ ($\sigma = \uparrow, \downarrow$). D'autre part, la validité du modèle à deux bandes a été clairement mise en évidence en utilisant le fait que les résistivités résiduelles d'alliages ternaires à base de nickel ne sont pas proportionnelles à chacune des concentrations en impuretés[7]; ceci est mis à profit pour déterminer les résistivités résiduelles ρ_{ir}^0 associées à chaque bande s_σ pour chaque impureté i . Les résultats que l'on obtient pour ρ_{ir}^0 par cette méthode sont en accord avec les résultats que l'on déduit des études sur les alliages binaires entre 4–40°K.

Nous nous proposons ici de déterminer les résistivités associées à chaque bande s_σ pour le nickel, le cobalt et les impuretés de transition dissoutes dans le nickel et le cobalt. Nous utiliserons une méthode basée sur la variation des écarts à la loi de Matthiessen en fonction de la concentration. Cette méthode, *valable à toute température*, permet de mettre en évidence un terme de mélange de spin. En séparant les contributions de chaque bande à la résistivité, nous pouvons montrer sans équivoque l'existence d'états liés virtuels $s \uparrow d \uparrow$ et l'existence d'un effet de période.

Après avoir présenté nos résultats expérimentaux (Section 1), nous les discutons de façon qualitative (Section 2). Puis nous exposons le modèle de conduction à deux bandes dans les alliages à base de métaux ferromagnétiques (Section 3), modèle que nous avons utilisé pour séparer les contributions de chaque bande dans les alliages à base de nickel et de cobalt à 77 et à 297°K (Section 4). Enfin, après avoir examiné la cohérence et la précision de la méthode employée (Section 5), nous proposons une interprétation des différents résultats obtenus (ordre de grandeur

des résistivités, effet de période...) (Section 6).

(1) Résultats expérimentaux

Les alliages ont été préparés par fusion directe dans un four à induction sous atmosphère d'argon purifié. Nous avons utilisé du nickel et du cobalt Koch-Light titrés à 99,998 pour cent. La pureté des éléments dissous est en général supérieure à 99,9 pour cent. Nous avons fabriqué des échantillons cylindriques d'un diamètre de 1,5 mm environ, et d'une longueur allant de 5 à 8 cm.

Tous les échantillons ont été recuits pendant 40 hr à 1000°C sous vide de 10^{-5} mm de mercure. Par refroidissement lent après recuit, les échantillons à base de cobalt ont été obtenus dans la phase hexagonale (à l'exception des CoHf et des CoZr qui cristallisent en phase cubique).

Les concentrations nominales en impuretés sont testées par les mesures de résistivité à 4°K: la dépendance en concentration est linéaire pour des concentrations allant jusqu'à 5 pour cent d'impureté pour la plupart des alliages de nickel et pour des concentrations en impuretés inférieures à 2 ou 3 pour cent pour la plupart des alliages de cobalt (le cas des alliages contenant du zirconium ou de l'hafnium étant mis à part, en raison de la très faible solubilité de ces éléments dans le nickel et le cobalt[26]).

Les mesures ont été faites en courant continu suivant une méthode potentiométrique classique. Compte-tenu des soudures, de l'imprécision sur les concentrations en impuretés et de l'ignorance où l'on est du traitement thermique idéal pour chaque type d'alliage, les résultats à 4°K sont donnés avec une précision de 5 à 6 pour cent. Ces résultats obtenus à 4°K sont représentés sur les Figs. 1 et 2 et sont discutés qualitativement dans le paragraphe suivant (Section 2).

(2) Discussion des résultats de résistivité résiduelle

Nous examinons d'abord le cas des alliages de nickel, puis celui des alliages de cobalt,

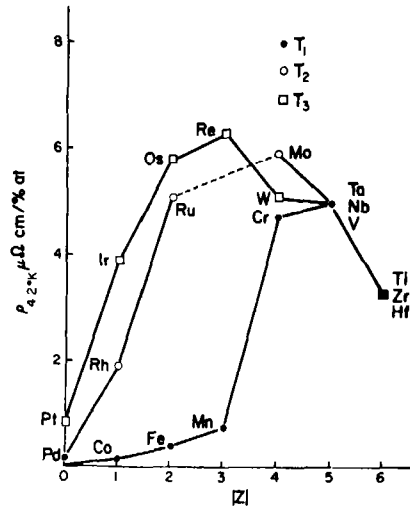


Fig. 1. Résistivités résiduelles des impuretés de transition dans le nickel. Les valeurs pour la première série de transition T_1 sont empruntées à Chen [8], les valeurs pour les NiV, NiNb, NiTa sont celles données par Arags *et coll* [9]. Pour le détail des résultats expérimentaux des autres alliages à 4°, 77° et 297°K aux diverses concentrations étudiées, voir Réf. [10].

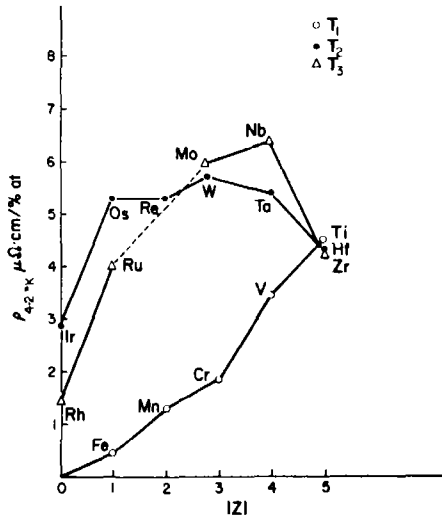


Fig. 2. Résistivités résiduelles des impuretés de transition dans le cobalt. Les résultats détaillés pour les différentes concentrations en impuretés et aux trois températures étudiées sont donnés dans la Réf. [10].

avant de discuter les résultats de façon générale en fonction de la théorie des états liés virtuels.

(a) *Alliages à base de nickel.* Les mesures de résistivité résiduelle [8] sur les alliages de nickel avec les éléments de la première série montrent que la résistivité est maximale pour l'alliage NiCr. Les mesures que nous avons faites sur les alliages de nickel avec les éléments des seconde et troisième séries de transition montrent que :

(i) Un fort accroissement de résistivité résiduelle est observé pour des valeurs de $|Z|$ plus petites ($|Z| = 2$ pour les impuretés de la deuxième série, $|Z| = 1$ pour la troisième série) :

(ii) La résistivité résiduelle ne dépend plus que de $|Z|$ pour $|Z|$ suffisamment grand ($|Z| = 5$ [9] et $|Z| = 6$) ; l'effet de période disparaît.

(b) *Alliages à base de cobalt.* Les mesures que nous présentons ne montrent pas de maximum pour les éléments de la première série : la résistivité croît régulièrement avec $|Z|$. Pour de petites valeurs de $|Z|$, les

[2] : lorsque le potentiel perturbateur du à l'impureté est suffisamment *répulsif*, un état lié $d \uparrow$ est extrait de la bande pleine du métal ferromagnétique fort (nickel ou cobalt). Cet état entre en résonance avec les états $s \uparrow$ pour former un état lié virtuel ; celui-ci modifie considérablement les propriétés de l'alliage lorsqu'il se situe au voisinage du niveau de Fermi. On observe alors :

(iii) Une décroissance de l'aimantation moyenne $\bar{\mu}(c)$ avec la concentration d'impuretés :

$$\frac{d\bar{\mu}}{dc} = -(Z+p)\mu_n$$

($p/2$ = nombre d'états $d \uparrow$ inoccupés);

(ii) Lorsque l'état lié traverse le niveau de Fermi, un maximum de densité d'états:

(iii) Un maximum de la résistivité résiduelle $\rho(s \uparrow)$ de la bande $s \uparrow$: en effet, celle-ci, étant due aux transitions $s-d$ induites par l'impureté, est proportionnelle à la densité d'états au niveau de Fermi sur le site de l'impureté $n_d(E_F, 0)$:

$$\rho(s \uparrow) = \frac{m^*}{N e^2} \frac{2\hbar}{h} \langle |V_{sd}|^2 \rangle_E n_d(E_F, 0),$$

m^* est la masse effective des électrons s et N le nombre d'électrons par atome. Cette formule est valable de façon générale pourvu qu'on néglige l'effet direct de potentiel d'impureté (c'est-à-dire les éléments de matrice V_{ss}).

(iv) Un renversement du signe du pouvoir thermoélectrique;

(v) Une large extension de la variation d'aimantation autour de l'impureté: ceci est dû à la grande extension de l'état lié $d \uparrow$ lorsque son énergie est assez voisine de celle du haut de la bande $d \uparrow$. Les mesures de diffraction neutronique et de champs hyperfins (RMN) permettent de montrer ce fait.

A cet égard les mesures de résistivités que nous présentons pour les alliages de nickel, ainsi que les mesures d'aimantation [11] de P.T.E [12], de RMN [13] et de diffraction neutronique [14] connues par ailleurs, montrant qu'un état lié apparaît d'autant plus facilement qu'une impureté de Z donné est plus lourde.

L'effet électrostatique n'est pas suffisant en général pour expliquer la structure électronique de ces alliages: la nature des couches d de l'impureté (extension, stabilité, couplage spin-orbite) joue donc un rôle important dans l'apparition des états liés virtuels. L'effet électrostatique devient prédominant pour des $|Z|$ élevés, puisqu'alors l'effet de période disparaît.

Dans le cas des alliages de cobalt, aucun maximum de résistivité n'apparaît, bien que les mesures d'aimantation [16, 18] suggèrent

l'existence d'états liés virtuels au voisinage du niveau de Fermi. L'équivoque des mesures de résistivité résiduelle provient de ce que l'on mesure à la fois la contribution des résistivités des électrons $s \uparrow$ et $s \downarrow$. Lorsque les bandes s_σ sont indépendantes, elles conduisent le courant en parallèle de sorte qu'on mesure une résistivité inférieure à la plus petite des résistivités $\rho(s_\sigma)$ ($\sigma = \uparrow, \downarrow$): si la résistivité des bandes $s \downarrow$ est très faible, le maximum de résistivité n'apparaît pas. Nous avons donc été amenés à séparer les diverses contributions pour tous les alliages de nickel et de cobalt à 77° et à 300°K. L'effet des états liés virtuels apparaîtra clairement dans $\rho(s \uparrow)$ (Section 6).

Notons enfin que, comme dans le cas des alliages de nickel, l'effet de période disparaît pour de grandes valeurs de $|Z|$.

(3) Conduction à deux bandes dans les alliages à base de métaux ferromagnétiques

Nous avons mesuré la résistivité de tous les alliages étudiés à 77 et à 297°K. Nous observons de forts écarts à la loi de Matthiessen $\Delta\rho(T) = \rho_{\text{all}}(T) - c\rho_0 - \rho_m(T)$: dans cette formule, $c\rho_0$ est la résistivité résiduelle de l'alliage de concentration atomique c , $\rho_{\text{all}}(T)$ et $\rho_m(T)$ sont respectivement les résistivités de l'alliage et de la matrice pure à la température T . Les écarts observés sont reportés dans les Figs. 3 et 4.

La loi de Matthiessen ($\Delta\rho(T) = 0$) suppose que les processus de diffusion.

(1) Ont lieu dans une seule bande ou dans plusieurs bandes.

(2) Sont indépendants.

(3) Elle suppose enfin qu'on peut définir un temps de relaxation pour chacun des processus de diffusion. On peut donc s'attendre *a priori* à de fortes déviations dans les métaux de transition de fait de l'existence de plusieurs bandes jouant des rôles différents à vis de la conduction (10 bandes d , 2 bandes s). De plus, dans les ferromagnétiques, de nombreux mécanismes de diffusion sont susceptibles d'être responsables de la résistivité: collisions

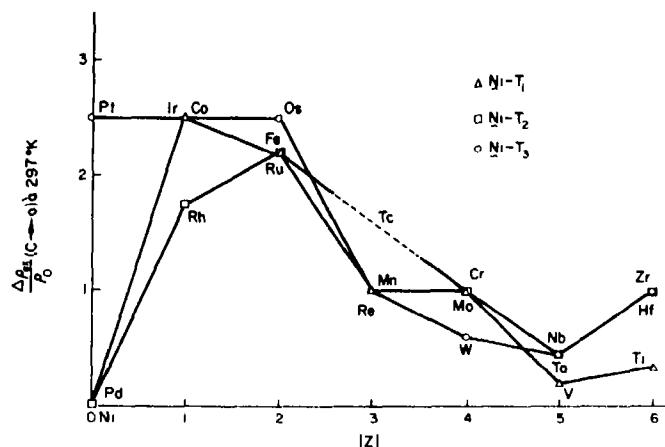


Fig. 3. Déviations à la loi de Matthiessen $\Delta\rho_{ex}$ à 297°K pour les alliages de nickel avec les métaux de transition. Les résultats pour la première série de transition sont empruntés à Farrell et Greig [4]. Comme $\Delta\rho_{ex}$ à 297°K dépend de c , on a extrapolé $\Delta\rho_{ex}$ à $c \rightarrow 0$.

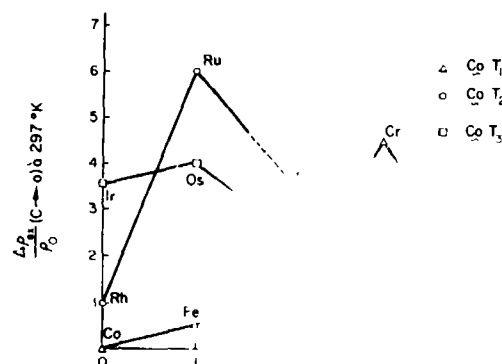


Fig. 4. Déviations à la loi de Matthiessen $\Delta\rho_{ex}$ à 297°K pour les alliages de cobalt avec les métaux de transition.

d'électrons avec ou sans renversement de spin, diffusion de Baber, transitions $s-d$ dues aux phonons etc. . . .

En l'absence d'une estimation correcte de la contribution des électrons $d \downarrow$ à la conduction, nous avons adopté un modèle de conduction à deux bandes $s \uparrow s \downarrow$. Ce modèle simplifié rend compte de façon suffisante des résultats que nous avons obtenus. Dans la suite de ce paragraphe, nous rappelons les formules utilisées précédemment [4] avant de présenter le principe de notre méthode de

séparation des résistivités associées à chaque sous-bande s_σ .

Si on suppose qu'il n'existe pas de processus de diffusion faisant passer les électrons d'une bande à l'autre, les conductibilités associées à chacune des bandes supposées seules s'ajoutent de sorte que la résistivité de l'alliage s'écrit:

$$\tilde{\rho}_{all} = \frac{(\tilde{\rho}_{m\uparrow} + c\tilde{\rho}_{0\uparrow})(\tilde{\rho}_{m\downarrow} + c\tilde{\rho}_{0\downarrow})}{\tilde{\rho}_{m\uparrow} + \tilde{\rho}_{m\downarrow} + c(\tilde{\rho}_{0\uparrow} + \tilde{\rho}_{0\downarrow})}. \quad (3.1)$$

Pour une bande σ ($\sigma = \uparrow, \downarrow$), $\tilde{\rho}_{m\sigma}$ repré-

sente la résistivité associée à *tous* les mécanismes de diffusion de la bande σ dans le métal pur, $\bar{\rho}_{0\sigma}$ représente la résistivité résiduelle de la bande σ supposée seule; elle inclut, de plus, les écarts à la loi de Matthiessen intervenant dans chaque bande σ ; si ces déviations ne sont pas nulles, $\bar{\rho}_{0\sigma}$ dépend de la température, soit parce que la structure électronique de l'impureté varie, soit parce que $\bar{\rho}_{0\sigma}$ inclut le terme de modification du spectre de phonons dû à l'impureté [25].

En fait, les bandes s_σ sont couplées par un certain nombre de mécanismes de diffusion. De façon générale, pour l'alliage, la résistivité s'écrit alors sous la forme:

$$\rho_{\text{all.}} = \frac{(\rho_{m\uparrow} + c\rho_{0\uparrow})(\rho_{m\downarrow} + c\rho_{0\downarrow}) + \rho_{\text{H}} [\rho_{m\uparrow} + \rho_{m\downarrow} + c(\rho_{0\uparrow} + \rho_{0\downarrow})]}{\rho_{m\uparrow} + \rho_{m\downarrow} + c(\rho_{0\uparrow} + \rho_{0\downarrow}) + 4\rho_{\text{H}}}, \quad (3.2)$$

en fonction d'une résistivité ρ_{H} caractérisant l'ensemble des phénomènes de couplage [4-6].

Nous adopterons cette formule proposée initialement par Campbell et Fert [4], en notant toutefois les points suivants:

(1). $\rho_{m\sigma} = \rho_{m\sigma} + \rho'_{\text{H}}$ ne désigne pas la résistivité de la matrice associée à la bande σ seule: elle en diffère par le terme ρ'_{H} qui représente l'effet de l'ensemble des termes de couplage interbande.

(2). $\rho_{0\sigma}$ inclut les termes de renormalisation dus à l'effet de l'impureté sur le couplage interbande.

(3). Dans cette formule, nous avons supposé que les termes de couplage interbande dus à l'impureté étaient négligeables.

Le problème est donc de déterminer les valeurs $\rho_{m\sigma}$, $\rho_{0\sigma}$ et ρ_{H} à partir de l'analyse des déviations par rapport à la loi de Matthiessen. Nous utiliserons ici le fait que, pour une température donnée, $\Delta\rho(c, T)$ n'est pas une fonction linéaire de la concentration. Nous supposerons par raison de simplicité dans la suite que les quantités $\rho_{0\sigma}$ ne varient pas beaucoup avec la température et nous négligerons cette variation: l'importance de

celle-ci doit être de l'ordre de grandeur de celle qu'on observe dans les métaux normaux; cette approximation est donc raisonnable sauf peut-être dans des cas pathologiques (alliages CoRh, Ru, Os) où il peut y avoir une variation explicite de la structure électronique de l'impureté avec la température. Dans ces conditions, nous devons trouver des valeurs des quantités:

$$\alpha = \frac{\rho_{0\downarrow}}{\rho_{0\uparrow}}, \mu = \frac{\rho_{m\downarrow}}{\rho_{m\uparrow}}, \rho_{\text{H}}$$

reproduisant la fonction $\Delta\rho(T, c)$ dans toute la gamme de concentrations pour laquelle les résistivités résiduelles sont proportionnelles

à la concentration. La validité de cet ajustement doit être démontrée en remarquant que (1) les quantités μ et ρ_{H} ne dépendent que de la matrice (2) α doit varier faiblement avec la température. Ces conditions sont suffisamment restrictives pour qu'on puisse déterminer sans ambiguïté les coefficients α , μ et ρ_{H} à 77°K. A cet égard, faisons les remarques suivantes:

(a) *Influence du coefficient μ sur les résultats expérimentaux.* Les valeurs de $\rho_{\text{all.}}$ sont assez sensibles à la valeur du coefficient μ . Ainsi, en supposant $\rho_{\text{H}} \approx 0$, la valeur de $\Delta\rho(0, T)$ détermine précisément α pour chaque valeur de μ (à l'aide d'une équation du second degré); on peut alors tracer les courbes $\Delta\rho(c, T)$ pour les différentes valeurs de μ choisies; le résultat montre que la variation de l'écart à la loi de Matthiessen avec la concentration est sensible au choix de μ (Fig. 5).

(b) *Nécessité d'introduire $\rho_{\text{H}} \neq 0$.* Le terme ρ_{H} est nécessairement non nul dans les alliages de nickel sans quoi on ne pourrait trouver par ce procédé une valeur de μ unique permettant de reproduire les courbes expérimentales $\Delta\rho(c, 77^\circ\text{K})$ pour ces alliages.

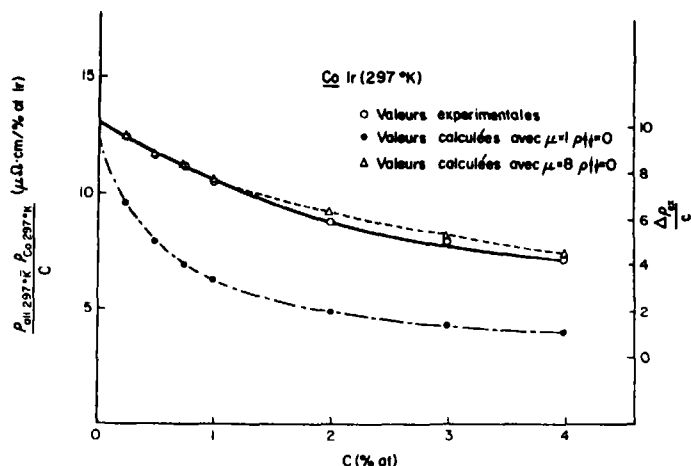


Fig. 5. $(\rho_{01} - \rho_{00})/\rho_0$ en fonction de c pour les CoIr à 297°K. ○ valeurs expérimentales; ● valeurs calculées avec $\mu = 1$, △ valeurs calculées avec $\mu = 8$

(4) *Séparation des contributions de chaque bande dans les alliages à base de nickel et de cobalt à 77 et 297°K*

(a) *Alliages de Nickel.* Nos mesures de résistivité sur les alliages ternaires à 4°K ont permis de déterminer les résistivités résiduelles ρ_{00} à 4°K du chrome et le cobalt dans le nickel. Nous supposons que les valeurs de ρ_{00} sont dépendantes de la température — le rapport σ n'excédant pas 10 pour cent [25]. Nous discutons, après séparation, la cohérence de cette hypothèse.

L'ensemble des résultats expérimentaux obtenus à 77°K ne peut s'interpréter qu'avec les valeurs suivantes:

$$\mu(\text{Ni}) = \rho_{m1}/\rho_{m1} = 2.6$$

$$\rho_{01}(\text{Ni}) = 0.3 \mu\Omega \cdot \text{cm} (T = 77^\circ\text{K})$$

Si on se donne $\rho_{01} = 0$, on doit choisir des valeurs de μ différentes pour les différents alliages à base de nickel ($\mu = 1.6$ pour NiCo, $\mu = 3.5$ pour NiRu, NiOs, par exemple) ce qui n'est pas physiquement acceptable.

Les résultats expérimentaux obtenus à 297°K permettent d'aboutir aux conclusions suivantes:

de même, c'est

rapport aux résistivités ρ_{m0} , elles ne sont pas suffisamment précises pour déterminer la valeur de ρ_{01} . En choisissant $\rho_{01} \approx 0$, l'ensemble des résultats expérimentaux s'interprète avec une valeur de μ comprise entre 1.60–1.86. Les valeurs trouvées pour ρ_{00} sont reportées dans les Figs. 7 and 8.

(b) *Alliages de cobalt.* Nous ne disposons pas à ce jour pour les alliages de cobalt des renseignements que nous avons sur les alliages de nickel. Nos mesures sur les CoIrRe [15] ne nous ont pas permis de déterminer le rapport α pour l'iridium et le rhénium dans le cobalt à 4°K (on sait seulement que $\alpha_{Ir} \approx \alpha_{Re}$). Des mesures sont en

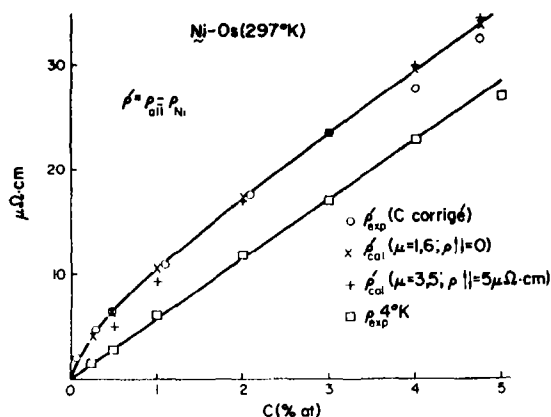


Fig. 6. ρ_{all} , ρ_{Ni} en fonction de c à 297°K pour les NiOs. La dépendance en c n'est pas linéaire, comme le montre la comparaison avec la courbe ρ_{exp} 4°K en fonction de c pour les mêmes alliages.

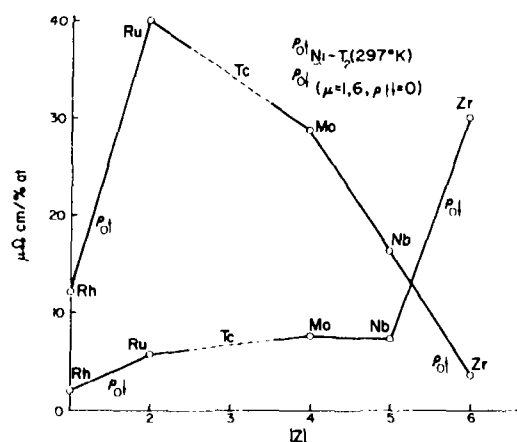


Fig. 7. ρ_{01} et ρ_{02} en fonction de $|Z|$ pour les alliages de nickel avec la deuxième série de transition à 297°K.

cours (déviations à la loi de Matthiessen sur les alliages binaires de cobalt entre 4–40°K, alliages ternaires CoFeIr à 4°K) qui devraient permettre de donner l'ordre de grandeur du terme de mélange de spin [16].

Nos propres mesures, dans la limite de précision de notre analyse, ne semblent pas imposer à 77°K l'existence d'un terme ρ_{η} de l'ordre de grandeur des $\rho_{m\sigma}$. Si l'on suppose ρ_{η} nul, on obtient un accord satisfaisant pour

tous les alliages avec une valeur $\mu = 11$ à 77°K. Si l'on suppose toutefois $\rho_{\eta} = 0,4 \mu\Omega \cdot \text{cm}$ à 77°K, comme pour le nickel, seule est changée substantiellement la valeur de α pour le fer dans le cobalt ($\alpha \approx 1$ pour $\rho_{\eta} = 0$, et $\alpha \approx 12$ pour $\rho_{\eta} = 0,4 \mu\Omega \cdot \text{cm}$).

L'étude des résultats expérimentaux à 297°K amène aux mêmes conclusions que dans le cas des alliages de nickel:

(i) ρ_{η} n'est pas très grand par rapport aux résistivités $\rho_{m\sigma}$: les écarts à la loi de Matthiessen à 300°K ne sont pas proportionnels à la concentration en impureté [10];

(ii) Les mesures expérimentales s'interprètent bien avec une valeur de ρ_{η} petite par rapport aux résistivités $\rho_{m\sigma}$. Si l'on suppose $\rho_{\eta} \approx 0$, on obtient un bon accord entre les valeurs expérimentales et les valeurs calculées à l'aide de $\mu = 8$, en attendant que des mesures ultérieures permettent de déterminer les valeurs précises des termes de mélange de spin à toute température. Les valeurs trouvées pour $\rho_{0\sigma}$ sont reportées dans les Fig. 9–11.

(5) Cohérence et précision de la méthode utilisée

Avant de discuter le sens physique des résultats obtenus, il convient d'examiner la cohérence et la précision de la méthode employée pour déterminer les différents paramètres: $\rho_{m\sigma}$, $\rho_{0\sigma}$ et ρ_{η} .

Dans tous nos calculs, nous avons supposé que les $\rho_{0\sigma}$ ne varient pas de plus de 10 pour cent entre 4–300°K en assimilant le cas d'une bande σ à celui d'un métal normal. Il faut vérifier si les valeurs obtenues sont cohérentes avec cette hypothèse, compte-tenu de la précision des mesures et des calculs.

(a) *Alliages de nickel*—(1) *Alliages de NiCo et NiCr*. Pour les alliages NiCo, nos mesures sur les alliages ternaires à 4°K nous ont donné $\alpha_{Co} \approx \rho_{01}/\rho_{01} \approx 20$. Campbell et Fert proposent la valeur $\alpha_{Co} = 30$ pour $4^\circ\text{K} \leq T \leq 40^\circ\text{K}$. Compte-tenu du fait que les résistivités mesurées sur ces alliages sont très faibles, l'erreur absolue dans la détermination des $\rho_{0\sigma}$ peut être assez importante, sans que l'on

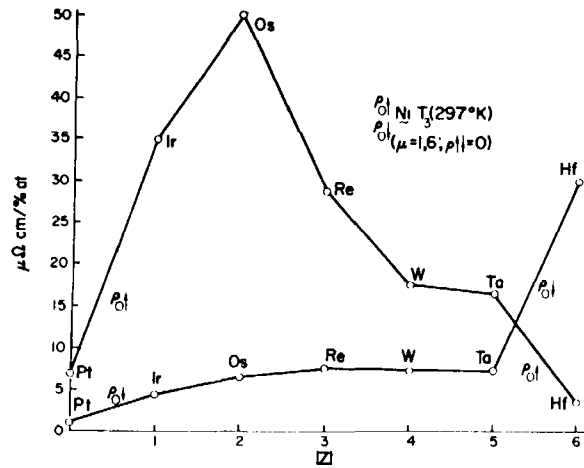


Fig. 8 $\rho_{0\uparrow}$ et $\rho_{0\downarrow}$ en fonction de $|Z|$ pour les alliages de nickel avec la troisième série de transition à 297 K

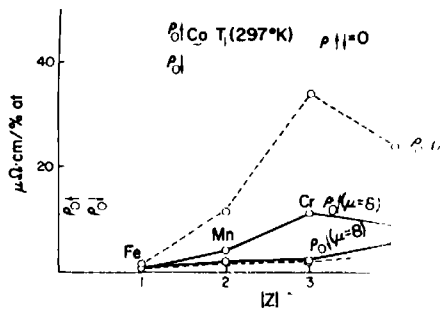


Fig. 9. $\rho_{0\uparrow}$ et $\rho_{0\downarrow}$ en fonction de $|Z|$ pour les alliages de cobalt avec la première série de transition à 297 K. Les valeurs des $\rho_{0\sigma}$ ($\sigma = \uparrow, \downarrow$) sont sensibles à la grandeur de μ , comme le montre la comparaison entre les $\rho_{0\sigma}$ calculés avec $\mu = 1$ et avec $\mu = 8$.

puisse en conclure à une variation notable des $\rho_{0\sigma}$ en fonction de la température.

Pour les alliages NiCr, on obtient.

	4°K	4 à 40°K	77°K	273°K
$\alpha_{\uparrow}$	0,36	0,38	0,32	0,34

Il semble que les écarts soient à attribuer à l'imprécision de la méthode de calcul employée à chacune des températures étudiées.

Si l'on compare aux valeurs expérimentales des alliages ternaires NiCoCr à 77 et à 297°K, les valeurs calculées avec $\rho_{0\sigma}$ (4°K) pour le cobalt et le chrome et les couples

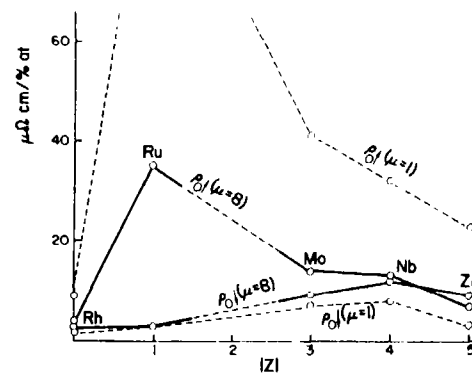


Fig. 10 $\rho_{0\uparrow}$ et $\rho_{0\downarrow}$ en fonction de $|Z|$ pour les alliages de cobalt avec la deuxième série de transition à 297°K.

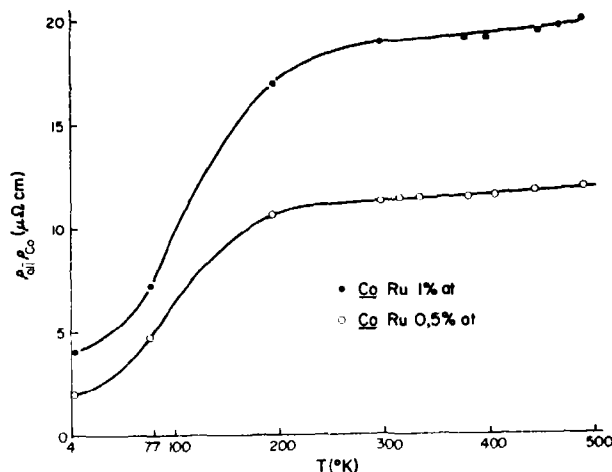


Fig. 12. ρ_{al}/ρ_{Co} en fonction de la température pour les alliages CoRu avec 0,5% at et 1% at de Ru. La saturation est déjà atteinte à la température ambiante.

(a) *Ordre de grandeur et variation de μ en fonction de la température.*

(1) Si la valeur de μ obtenue pour la cobalt est en bon accord avec le modèle de Mott (prédominance des transitions $s-d$), $\rho_{m\uparrow} \approx \rho_{m\downarrow}$, c'est-à-dire $\mu \approx 1$, beaucoup plus faible obtenue ; semble montrer que les termes magnon jouent un rôle important à température ambiante. En effet, les matrices associées à chaque bande s'écrivent sous la forme :

$$\begin{aligned} \rho_{m\uparrow} &= \rho_{i\uparrow} + \rho'_{i\uparrow} \\ \rho_{m\downarrow} &= \rho_{i\downarrow} + \rho'_{i\downarrow} + \rho''_{i\downarrow} + \rho_{i\downarrow d}. \end{aligned} \quad (6.1)$$

Dans ces formules, ρ_{ir} est la résistivité idéale de chaque bande s_r supposée seule ($\rho_{i\uparrow} \approx \rho_{i\downarrow}$);

$\rho_{i\downarrow d}$ est la partie $s-d$ de la résistivité idéale;

$\rho''_{i\downarrow}$ représente le terme de Baber[5];

$\rho'_{i\uparrow}$ est un terme de couplage dû aux interactions électron-magnon[6].

D'après les estimations raisonnables, les

termes $\rho''_{i\downarrow}$ et $\rho_{i\downarrow d}$ sont bien supérieurs à la résistivité ρ_{ir} . Le résultat obtenu pour le nickel ($\rho_{m\downarrow} \approx 1.6 \rho_{m\uparrow}$ à 300°K) ne peut donc s'interpréter qu'en admettant que le terme $\rho_{i\downarrow d}$ est du même ordre de

terme de couplage $\rho'_{i\uparrow}$ est le plus dominant. Nous obtenons à 77°K pour le nickel un terme dont l'ordre de grandeur est identique à celui qui a été obtenu par Campbell et Fert par une autre méthode[4].

(c) *Variation des résistivités $\rho_{0\downarrow}$ en fonction de $|Z|$. Effet de période.* La position des maxima des $\rho_{0\downarrow}$ en fonction de $|Z|$ montre sans ambiguïté un effet de période aussi bien pour les alliages de cobalt que pour les alliages de nickel: pour les deuxième et troisième séries, les maxima indiquent que l'état lié virtuel traverse le niveau de Fermi pour le ruthénium et l'osmium ($|Z| \approx 1$ pour le

cobalt, $|Z| = 2$ pour le nickel); alors que pour la première série de transition, le maximum apparaît au chrome ($|Z| = 3$ pour le cobalt, et $|Z| = 4$ pour le nickel).

Ces indications sont cohérentes avec les renseignements fournis sur la structure électronique de ces alliages par les mesures d'aimantation [11-17], de pouvoir thermo-électrique [12-20], de diffraction de neutrons [14] et de RMN [13-19].

(d) *Lien entre les mesures d'aimantation et de résistivité.* On peut établir un lien quantitatif entre les valeurs de p calculées à partir des mesures d'aimantation d'après la formule:

$$\frac{d\bar{\mu}}{dc} = -(Z + p)\mu_B, \quad (6.2)$$

et les valeurs de $\rho_{0\uparrow}$ déterminées à partir de l'analyse des déviations à la loi de Matthiessen.

Dans la mesure où l'état lié virtuel n'est pas au voisinage immédiat de la bande d , la valeur de p est donnée en fonction de $x = (E_F - E_l)/\Delta$, ($E_F - E_l$) représentant la position du niveau lié par rapport au niveau de Fermi et 2Δ étant la largeur de la résonance $s_{\uparrow} d_{\uparrow}$ par la relation:

$$5 - \frac{p}{2} = \int_{-x}^{x_F} n_d(E) dE = \frac{5}{11} \left[\text{Arctg } x + \frac{11}{2} \right]. \quad (6.3)$$

En outre, la résistivité dans la bande $\uparrow$ due à l'état lié virtuel est donnée par:

$$\rho_{0\uparrow}(l=2) = A \sin^2 \delta(E_F) = \frac{A}{1+A^2}, \quad (6.4)$$

où A , pour un gaz d'électrons libres, est:

$$A = \frac{2011}{n_{\uparrow} k_F}. \quad (6.5)$$

$n_{\uparrow}$ désignant le nombre d'électrons $s_{\uparrow}$ par atome. Nous pouvons donc comparer les valeurs de $\rho_{0\uparrow}$ obtenues à l'aide de notre méthode de séparation et les valeurs de

$\rho_{0\uparrow}(l=2)$ calculées à partir des mesures d'aimantation à l'aide de la formule:

$$\rho_{0\uparrow}(l=2) = \frac{A}{1 + tg^2(11/2 - p11/10)}. \quad (6.6)$$

Nous examinons successivement les cas des alliages de nickel et de cobalt.

(1) *Alliages de nickel.* Pour le chrome dans le nickel, on a $p = 8$ et $\rho_{0\uparrow} = 19 \mu\Omega \cdot \text{cm}/\% \text{ at.}$ En calculant le coefficient A à partir de ces valeurs, on obtient $A_{\text{calc}} = 55 \mu\Omega \cdot \text{cm}/\% \text{ at.}$ Si l'on calcule le coefficient A à partir de la formule d'électrons libres, on obtient $A_l = 73,6 \mu\Omega \cdot \text{cm}/\% \text{ at.}$ L'écart entre ces deux valeurs de A peut s'interpréter à partir de l'anisotropie de la surface de Fermi $s_{\uparrow}$.

Si on admet la valeur de A calculée à l'aide des résultats sur le chrome, on peut alors calculer $\rho_{0\uparrow}(l=2)$ pour tous les autres éléments dans le nickel à partir des valeurs de p données par les mesures d'aimantation. Quand l'état lié virtuel traverse le niveau de Fermi (valeurs de p voisines de 5), on peut négliger les déphasages correspondant à $l \neq 2$; on trouve effectivement pour le ruthénium et l'osmium un bon accord quantitatif entre les valeurs calculées $\rho_{0\uparrow}(l=2)$ et les valeurs de $\rho_{0\uparrow}$ obtenues par analyse des déviations à la loi de Matthiessen (Fig. 13).

Par contre, lorsque l'état lié virtuel est bien au-dessus du niveau de Fermi ($|Z|$ grand), les termes $l \neq 2$ fournissent une contribution non négligeable à la résistivité, et les valeurs de $\rho_{0\uparrow}$ sont nettement plus grandes que les valeurs calculées $\rho_{0\uparrow}(l=2)$.

(2) *Alliages de cobalt.* En admettant que pour les CoRu et CoOs (où $p \approx 5$) on ait $\rho_{0\uparrow} \approx \rho_{0\uparrow}(l=2)$, on obtient $A = 35 \mu\Omega \cdot \text{cm}/\% \text{ at.}$ Ce résultat est assez voisin de la valeur $A_l = 34 \mu\Omega \cdot \text{cm}/\% \text{ at.}$ calculée à partir d'un modèle d'électrons libres en supposant que le cobalt possède 0,35 électrons $s_{\uparrow}$ par atome. On admet la valeur $A = 35 \mu\Omega \cdot \text{cm}/\% \text{ at.}$ et si on compare alors les valeurs de $\rho_{0\uparrow}(l=2)$ calculées à partir des mesures d'aimantation avec les valeurs de $\rho_{0\uparrow}$ déterminées à partir

des mesures de résistivité, on obtient un accord de plus en plus approximatif à mesure que l'état lié virtuel s'éloigne du niveau de Fermi[10].

(e) *Variation des $\rho_{0\downarrow}$ en fonction de $|Z|$.* Les valeurs de $\rho_{0\downarrow}$ sont à peu près constantes; elles ne dépendent pas notablement ni de la

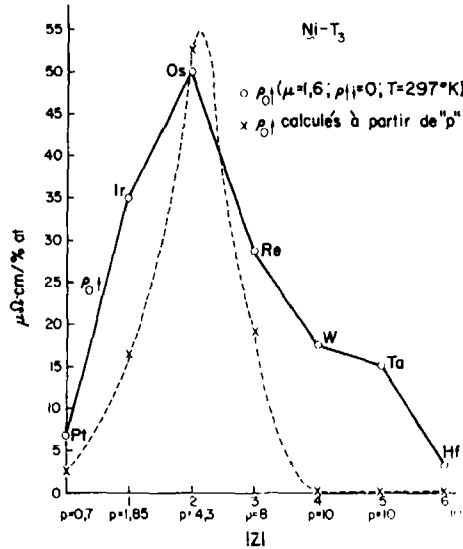


Fig. 13 Comparaison entre les $\rho_{0\downarrow}$ calculés à partir de mesures d'aimantation et les $\rho_{0\downarrow}$ déterminés à partir de mesures de résistivité pour les alliages de la troisième série de transition.

série ni de $|Z|$, sauf pour les valeurs extrêmes de $|Z|$ ($Z = 0$ et $|Z| = 5$ ou 6). En l'absence d'un calcul complet de la structure électronique de ces alliages, on ne peut comparer ces valeurs à des valeurs théoriques de la résistivité dans la bande $\downarrow$. Mais on peut utiliser la formule de Gomes[21] pour déduire des $\rho_{0\downarrow}$ une valeur de V_{sd} .

En négligeant la diffusion s - s , en traitant les électrons s en liaisons fortes et en supposant le potentiel perturbateur localisé, Gomes obtient:

$$\rho_{0\downarrow} = \sum_i \frac{2\hbar m |V_{sd}|^2 n_d(E_F) + n_s(E_F) |V_{sd}|^4 [F_i(E_F)^2 + \hbar^2 n_i(E_F)^2]}{n_i e^2 [1 - V_{0\downarrow} F_i(E_F)]^2 + \hbar^2 n_i(E_F)^2 V_{0\downarrow}^2}$$

où $n_i(E_F)$ et $F_i(E_F)$ sont respectivement la densité d'états correspondant à l'orbitale d_i ($i = 1, \dots, 5$) et sa transformée de Hilbert.

L'approximation de liaisons fortes utilisée pour représenter la bande s étant très douteuse, la formule de Gomes ne peut donner qu'un ordre de grandeur de la résistivité. En utilisant les valeurs self-consistantes de $V_{0\downarrow}$ calculées par Hayakawa[22] et Demangeat[23] pour les éléments de la première série de transition dans le nickel et en introduisant dans la formule de Gomes les valeurs de $\rho_{0\downarrow}$ obtenues par notre méthode de séparation, on obtient pour V_{sd} les valeurs données par le tableau suivant (V_{sd} exprimé en eV):

	C_0	I_s	M_n	C_s	V
V_{sd}	2.2	3.1	4.3	2.8	2.5

Les valeurs de V_{sd} ainsi calculées, sensiblement constantes pour la première série de transition dans le nickel, semblent relativement grandes; en particulier, elles entraînent, pour les états liés virtuels s - d , des largeurs

bandes d'onde k données par la fonction de bas de bande. On peut montrer, sous certaines hypothèses restrictives, que le potentiel perturbateur $V_p(r)$ introduit par une impureté B de même valence que la matrice A s'écrit:

$$V_p(r) = \begin{cases} \Delta E_0 + V_c(r) & r \leq r_c \\ V_c(r) & r \geq r_c \end{cases}$$

où r_s est le rayon de la sphère de Wigner;

$\Delta E = E_B - E_A$ est la différence des énergies E_B et E_A de bas de bande dans les métaux B et A ;

$V_e(r)$ est le potentiel d'écran introduit autour de cette perturbation.

L'effet de période peut être étudié de façon analogue dans le cas des métaux de transition paramagnétiques. On admet que les électrons d participant à l'écran sont bien représentés par un modèle de liaisons fortes [2]. Dans le cas d'une bande non dégénérée, on montre que le potentiel perturbateur $V_p(r)$ introduit par une impureté (substitutionnelle) B située à l'origine 0 s'écrit sous la forme:

$$Z \neq 0 \begin{cases} V_p(r) = \Delta E_0^* + U^1 \delta \rho^1(0) & r < r_s \\ V_p(r) = \delta v_r(r) + V_e(r) & r \gg r_s \end{cases}$$

où ΔE_0^* est relié aux énergies des états atomiques (E_1, E_B) et aux potentiels moyens dans l'alliage (α_B) et dans la matrice (α_A) créés dans la cellule centrale 0 par les autres atomes:

$$\Delta E_0^* = E_B + \alpha_B - (E_A + \alpha_A);$$

$\delta v_r(r)$ représente la différence des potentiels de coeur entre l'impureté et la matrice; $\delta \rho^1(0)$ désigne l'écart à la neutralité de la densité électronique totale sur la cellule de l'impureté; U^1 est l'énergie qu'il faut fournir pour amener un électron supplémentaire sur l'impureté; $V_e(r)$ est le potentiel d'écran en dehors de la cellule centrale.

Lorsqu'on passe d'une impureté de la première série à une impureté de la troisième série, la différence de charge électronique Z et la configuration des électrons s étant supposées inchangées, $E_B - E_A$ croît, tandis que U^1 décroît. ΔE_0^* et U^1 introduisent un potentiel supplémentaire répulsif et varient de telle sorte que la perturbation électronique due à l'effet de période soit de plus en plus importante. Ceci est suffisant pour favoriser l'apparition d'états liés virtuels pour de faibles valeurs de $|Z|$ [23].

Le problème de l'effet de période dans le cas des métaux de transition ferromagnétiques est plus compliqué à traiter, car il faut résoudre simultanément l'écran dans la bande $\uparrow$ et dans la bande $\downarrow$. En traitant $V_p(r)$ comme une perturbation pour les cellules autres que celles de l'impureté, Demangeat a pu montrer que la variation de ΔE_0^* et de U^1 est suffisante pour faciliter l'apparition d'états liés virtuels. Cependant, le calcul quantitatif de cet effet n'est possible qu'après une étude de l'effet des corrélations *intra-atomiques* et *interatomiques* sur l'écran créé autour d'une impureté.

CONCLUSION

La présente étude montre sans ambiguïté, dans les alliages de nickel et de cobalt, (1) l'existence d'états liés virtuels, (2) l'existence d'un effet de période, (3) l'existence d'une conduction à deux bandes, avec un terme de mélange de spin important à 77°K dans le cas du nickel.

Elle a permis la détermination *quantitative* des résistivités résiduelles associées à chacune des bandes.

Des mesures en cours devraient permettre de préciser l'importance du terme de mélange de spin $\rho_{\uparrow\downarrow}$ à toute température dans les alliages de nickel et dans les alliages de cobalt ainsi que l'évolution en fonction de la température des résistivités résiduelles $\rho_{0\sigma}$ et des résistivités $\rho_{m\sigma}$ du nickel et du cobalt: une telle étude des phénomènes de transport dans les ferromagnétiques peut donc permettre de mieux comprendre l'origine du magnétisme dans les métaux de transition.

Remerciements — Nous remercions Madame M. C. Cadeville dont l'aide nous a été précieuse, ainsi que les Dr D. Greig, I. A. Campbell et A. Iert, qui nous ont fait connaître les résultats de leurs recherches en cours sur les alliages de nickel.

REFERENCES

1. CADEVILLE M. C. et DURAND J., *Solid State Commun.* **6**, 399 (1968).
2. FRIEDEL J., *Nuovo Cim. Suppl.* **7**, 287 (1958); *J. Phys. Radium*, **23**, 692 (1962).

3. MOTT N. F., *Proc. phys. Soc.*, **47**, 571 (1935); *Proc. R. Soc. A* **153**, 699 (1936 a); **156**, 368 (1936 b).
4. CAMPBELL I. A., FERT A. and POMEROY A. R., *Phil. Mag.* **15**, 977 (1967).
FERT A. and CAMPBELL I. A., *Phys. Rev. Lett.* **21**, 1190 (1968).
FARRELL T., *Phys. Rev.* **174**, 564 (1968).
FARRELL T. and GREIG D., *J. phys. C. (Proc. Phys. Soc.)*, Serie 2, **1**, 1359 (1968).
SCHWERER F. C., CONROY J. W. and ARAJS S., *J. Phys. Chem. Solids* **30**, 1513 (1969).
5. BOURQUARD A., DANIEL E. et FERT A., *Phys. Lett.*, **26A**, 260 (1968), BABER W. G., *Proc. R. Soc. A* **158**, 383 (1937).
6. MANNARI I., *Prog. theor. Phys.* **22**, 335 (1959).
7. LEONARD P., CADEVILLE M. C., DURAND J. et GAUTHIER F., *J. Phys. Chem. Solids*, **30**, 2169 (1969).
8. CHEN C. W., *Phys. Lett.*, **7**, 16 (1963).
9. ARAJS S., *J. appl. Phys.*, **32**, 97 (1961); CHESSIN H., ARAJS S. and COLVIN R. V., *J. appl. Phys.*, **35**, 2419 (1964); ARAJS S., CHESSIN H. and COLVIN R. V., *Phys. Status Solidi*, **7**, 1009 (1964).
10. DURAND J., Thèse de troisième cycle, Strasbourg (1969).
11. WEISS P. et LORRER R., *Annls. Phys.*, **12**, 279 (1929); MARIAN V., *Annls. Phys.*, **7**, 459 (1937), SHULL C. G. and WILKINSON M. K., *Phys. Rev.* **97**, 304 (1955), CRANGI F. J. and PARSONS D., *Proc. R. Soc. Lond.*, **255**, 509 (1960).
12. FARRELL T., GREIG D. and ROWLANDS I. A., *Low Temperature Physics L.T. II*, (Edited by J. F. ALLEN, D. M. FINLAYSON and D. M. MCCALL), Vol. 2, p. 1074, St ANDREWS Scott (1968). GREIG D., Leeds (communication).
13. BENNETT J. H. and STREFFER *Phys.*, **33**, 1093 (1962), STREFFER *Phys.*, **33**, 1093 (1962), STREFFER *Phys. Rev.* **139**, 1329 (1966); STREFFER R. I., *Phys. Rev.* **174**, 591 (1968), KUBO H., KONTANI T., *J. phys. Soc. Japan* **22**, 929 (1967).
14. LOW G. G. F. and COLLINS M. F., *Phys. Rev. Lett.* **11**, 1174 (1968); COMLY J. B., HOLDEN T. M. and LOW G. G. E., *J. Phys. C. (Proc. phys. Soc.)*, Serie 2, **1**, 458 (1968).
15. DURAND J., (non publié).
16. IOEGEL B., Strasbourg (communication privée).
17. PAYRAUDEAU L., Strasbourg (communication privée).
18. CRANGI F. J., *Phil. Mag.* **2**, 659 (1957); LOMER W. M. and MARSHALL W., *Phil. Mag.* **3**, 185 (1958).
19. LA FORCE R. C., RAVITZ S. F. and DAY G. F., *Phys. Rev. Lett.* **6**, 226 (1961); KOI Y., TSUJIMURA A., HIHARA T. and KISHIDA T., *J. phys. Soc. Japan*, **16**, 574 (1961); KOBAYASHI S., ASAYAMA K. and ITOH J., *J. phys. Soc. Japan*, **21**, 65 (1966); RIEDI P. C., SCURLOCK R. G. and WILMHURST T. H., *J. Phys. C. (Solid St. Phys.)*, Serie 2, **2**, 259 (1969).
20. CADEVILLE M. C. et ROUSSEI J., Strasbourg (communication privée).
21. GOMES A. A., *J. Phys. Chem. Solids* **27**, 451 (1966).
22. HAYAKAWA H., *Progr. theor. Phys.*, **37**, 213 (1967).
23. DEMANGEAT C., Thèse de troisième cycle, Strasbourg (1969).
24. RIEDER J., *Can. J. Phys.* **34**, 1190 (1956).
25. KAGAN Yu. and ZHERNOV A. P., *Soviet Phys. JETP*, **23**, 737 (1966).
26. HANSEN M., *Constitution of Binary Alloys*, McGraw-Hill, New York (1958). ELLIOTT R. P., *Constitution of Binary Alloys*, 1st Suppl., McGraw-Hill, New York (1965).

TECHNICAL NOTES

Quench enhanced ordering of Fe Ni₃

(Received 5 January 1969; in revised form 3 June 1970)

THE EFFECT of an excess of vacancies introduced by quenching on ordering of Fe Ni₃ has been studied by resistivity measurements. In this alloy the order disorder transformation is very sluggish even at high temperatures: the annealing time required for complete order is about two weeks at 490°C and very little ordering is observed below 400°C [1, 2].

The present results on ordering enhancement due to quenching are of interest for the comparison with similar effects obtained by other authors, in particular: the formation of order enhanced by neutron irradiation on Fe Ni [3, 4]; the changes in magnetic properties due to directional order also enhanced by irradiation on several Fe Ni alloys close to Fe Ni₃ [5, 6]; and the formation of order enhanced by quenching on Cu₃Au [7].

The only previous study on ordering enhancement obtained by quenching on Fe Ni₃ was performed by Gomankov *et al.* [8] examining the superlattice lines by x-ray diffraction after annealing at 400 and 450°C. At these temperatures, however, vacancies are likely to have disappeared to a large extent and therefore their contribution to ordering should be somewhat limited.

The present results refer to annealing experiments, performed after quenching, in a lower temperature region, i.e. between 100 and 300°C, where the vacancy contribution to diffusion enhancement has the major effect.

The alloy (79.95 Ni and 24.05 Fe) was prepared by vacuum melting in a small induction furnace. The oxygen content, which can strongly affect the rate of ordering [10],

was found to be very small, of the order of 50 ppm. The specimens, in form of strips 0.2 mm thick and 120 mm long, were quenched into an iced brine bath from increasing temperatures using a vertical furnace with H₂ atmosphere. The cooling rate measured by oscilloscopic recording was about $0.5 \times 10^{+4}$ °C/sec. The resistivity was measured at 20 ± 1 °C with a double Kelvin bridge. The isothermal annealings were performed in a salt bath stabilized at ± 1 °C. The samples were contained in an iron tube filled with Argon atmosphere directly plunged into the salt bath. By this method the equilibrium temperature was reached in about 2 min.

The maximum resistivity change is reported in Fig. 1 as a function of the quenching temperature. The fact already observed by Beni *et al.* [7, 8] that for quenching temperatures above $0.8 T_m$ (where T_m is the melting

resistivity change observed

is controlled essentially by the change in the vacancy concentration in the alloy.

In Fig. 2 are given the isothermal changes of resistivity as a function of annealing time for a quenching temperature of 1000°C. As is seen some resistivity changes are already observed at temperatures as low as 100°C according to the fact that in Nickel single vacancies begin to be mobile at this temperature, as shown by the relaxation peak observed by Chamberod *et al.* [11].

In Fig. 3 the resistivity changes observed

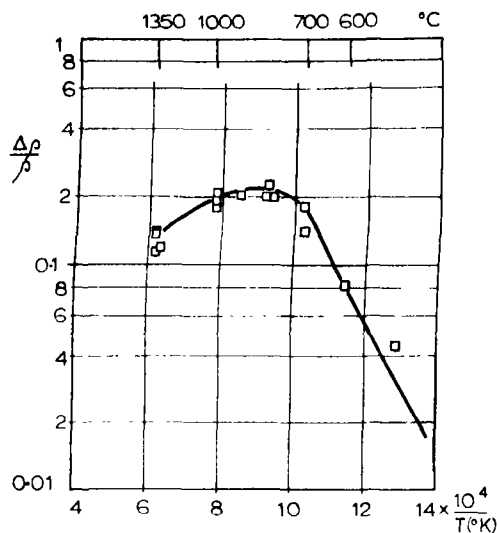


Fig. 1. Resistivity change after annealing 24 hr at 300°C due to ordering in FeNi₃ as a function of quenching temperature.

on specimens quenched from 1000°C and then annealed are plotted as a function of the annealing temperatures (for a constant annealing time of 14 hrs). The complete recovery of resistivity is observed between 490 and 510°C, in accordance with the

transition temperature of the FeNi₃ order disorder transformation.

The maximum observed change of resistivity is $4.1 \mu\Omega \text{ cm}$ ($\Delta\rho/\rho_0 \approx 0.25$), after 24 hrs at 340°C ($3.5 \mu\Omega \text{ cm}$ after 1 hr). Kaya[1] has observed a maximum resistivity change of $9 \mu\Omega \text{ cm}$ after a treatment of two weeks at 490°C, which can be supposed to have completely ordered the specimens. The amount of order which can be obtained by vacancy motion is thus, by comparison[2, 12], about 60 per cent. This value, is rather large and in agreement with the fact that, if vacancies make about 10^8 jumps before annealing to sinks, a concentration of vacancies of the order of 10^{-5} should be large enough to give long range ordering effect not too far from unity.

The isothermal annealing curves of Fig. 2 show a kinetics of the first order only for the early stages of ordering, typically at lower temperatures.

In conclusion it is seen that long range ordering can be obtained to a fairly large extent down to temperatures of about 300°C ($T/T_m \approx 0.35$) by the sole presence of vacancies introduced by quenching. However,

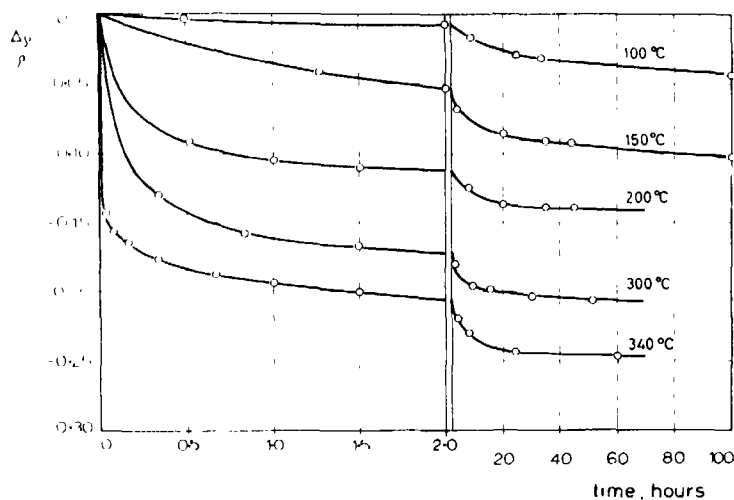


Fig. 2. Isothermal changes of resistivity, after quenching, as a function of annealing time (Quenching temperature: 1000°C).

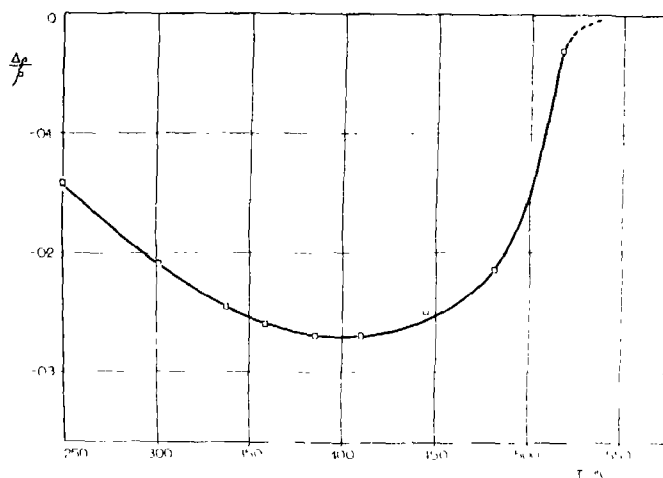


Fig. 3. Maximum resistivity change observed on FeNi, quenched from 1000°C after isothermal ordering at increasing temperatures (annealing time 14 hr)

from the comparison with the experimental results on neutron irradiated specimens, one may also conclude that not all the effects observed by irradiation can be obtained by quenching. This seems reasonable since during irradiation also other diffusion processes are active[6,13], and, furthermore, the vacancy concentration is much larger.

Istituto Elettrotecnico Nazionale
G. Ferraris,
Gruppo Nazionale di Struttura della
Materia del CNR,
Torino,
Italy

8. BENCI S., GASPARRINI G., GERMAGNOLI E. and SCHIANCHI G., *J. Phys. Chem. Solids* **26**, 2059 (1965).
9. GOMANKOV V. I., PUZEY J. M. and LOSHMANOV A. A., *Fiz. Metal. metallovd* **2**, 128 (1966).
10. NESBITT F. A., BATTERMAN B. W., FULLERTON I. D. and WILLIAMS A. J., *J. appl. Phys.*

REFERENCES

1. KAYA S., NAKAYAMA M. and SAITO H., *Proc. Phys. Math. Soc. Japan* **25**, 179 (1943).
2. WAKELIN R. J. and YATES E. I., *Proc. R. Soc.* **66B**, 221 (1953).
3. MARCHAND A. and CHAMBEROD A., *C. R. Acad. Sci. (Paris)* **261**, 8113 (1965).
4. NEEL, I., PAULLEVE J., PAUTHIENET R., LAUGIER J. and DAUTREPPE D., *J. appl. Phys.* **35**, 873 (1964).
5. SCHINDLER A. J. and WILLIAMS C. M., *J. appl. Phys.* **35**, 877 (1964).
6. SCHINDLER A. J., KERNOHAN R. H. and WEERTMAN J., *J. appl. Phys.* **35**, 2640 (1964).
7. BENCI S., GASPARRINI G., and GERMAGNOLI E., *Nuova Cim.* **31**, 1165 (1964).

Olivine-spinel transformation in MgMnGeO_4 , FeMnGeO_4 and CoMnGeO_4

(Received 1 June 1970)

BERNAL[1] and Jeffreys[2] first suggested that olivine might transform to a denser spinel structure under the high pressure existing deep within the earth's mantle. Such a transformation would be of considerable significance. This suggestion had been stimulated by Goldschmidt's[3] observation that the compound Mg_2GeO_4 displayed olivine and

*Istituto di Fisica dell'Università, Ferrara.

spinel polymorphs. Support for the Jeffreys-Bernal hypothesis emerged when Ringwood [4] found that the olivines Fe_2SiO_4 , Ni_2SiO_4 and Co_2SiO_4 could be transformed to spinel structures at pressures of 20 to 70 kb (1000°C) and that the transformations were accompanied by density increases of about 10 per cent. The geophysical significance of the olivine-spinel transformation was confirmed by Ringwood and Major's [5, 6] demonstration that olivines in the composition range Fe_2SiO_4 to $(\text{Mg}_{0.8}\text{Fe}_{0.2})_2\text{SiO}_4$ transformed to spinels at very high pressure. Blasse [7] has also observed an olivine-spinel transformation in LiMgVO_4 .

In the course of an investigation [8] of high pressure transformations of spinels into the strontium plumbate structure and of the solid solubility of Mg^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} and Si^{4+} in the high pressure strontium plumbate modification of Mn_2GeO_4 [9], we have discovered

three new olivine-spinel transformations. In view of the geophysical and crystallographic significance of this class of structural transformation, the present brief account has been prepared.

The previously unreported olivines MgMnGeO_4 and CoMnGeO_4 were prepared as well crystallized single phases by intimately mixing the pure oxide components (MgO , Mn_3O_4 , Co_3O_4 , GeO_2) in the required proportions, pelletizing, and sintering at 1300 and 1100°C respectively for 24 hr followed by regrinding and reheating. The olivine FeMnGeO_4 , also unreported, was prepared from an intimate mixture of Fe_2O_3 , Fe metal powder, Mn_3O_4 and GeO_2 in the correct proportions. The pelletized mixture, wrapped in platinum foil, was heated in a sealed, evacuated silica tube containing a small amount of metallic iron powder as a buffer for oxygen. Reaction at 950°C for 24 hr gave better than 95 per cent of the olivine FeMnGeO_4 . Precision lattice parameters for these three olivines were determined by diffractometer methods, with KCl as an internal standard.

Samples of the olivines were pressed in a single stage, high pressure-high temperature apparatus [6] operated at 35 kbars at 1200°C for 2 hr. Experimental procedures have been described elsewhere [10]. After completion

Table 1. Unit cell dimensions of some olivines and their high pressure spinel polymorphs (± 0.003 Å)

	a_0	Olivine b_0	c_0	Spinel a_0
MgMnGeO_4	4.982	10.559	6.181	8.399
FeMnGeO_4	5.010	10.641	6.210	8.468
CoMnGeO_4	4.991	10.649	6.195	8.426

Table 2. Parameters of olivine-spinel transformations

Compound	Ref	Transition Pressure, kbar	Temp. °C	Molar volumes, cm^3		Density increase, %
				Olivine	spinel	
Mg_2GeO_4	3, 4	0	820	45.87	42.35	8.3
Fe_2SiO_4	4	49	1000	46.39	42.03	10.4
Ni_2SiO_4	4	31	1000	42.51	39.17	8.5
Co_2SiO_4	4	70	900	44.56	40.58	9.8
Mg_2SiO_4 [a]	6	125	1000	43.79	39.58	10.6
MgMnGeO_4 [b]		(35) [c]	1100	48.97	44.62	9.8
FeMnGeO_4 [b]		(35) [c]	1100	49.85	45.73	9.0
CoMnGeO_4 [b]		(35) [c]	1100	49.23	45.05	9.3
LiMgVO_4	7	—	—	44.71	42.58	5.0

[a] Data obtained by extrapolation and refer to metastable Mg_2SiO_4 .

[b] This work.

[c] Brackets denote synthesis pressure for spinel. Equilibrium pressures are lower.

of each experimental run the temperature was quickly lowered to below 100°C, and the pressure then reduced. The samples were removed from the apparatus and examined by X-ray diffraction, using a Debye-Scherrer camera of 114 mm. dia. In each case, complete transformation to a spinel structure was observed, and even in the case of FeMnGeO_4 , no additional lines could be observed in the powder patterns after long exposures. The spinel lattice parameters given in Table 1 were obtained after applying film shrinkage corrections and extrapolating the unit cell values to $2\theta = 180^\circ$, making use of back angle reflections and appropriate extrapolation functions[11].

These new compounds provide a substantial extension of known olivine-spinel transformations, Table 2. The density increases are similar to those previously observed, as expected for the transformation of one structure type to another[12].

A. F. RINGWOOD
A. I. REID

Department of Geophysics and Geochem
Australian National University and
Division of Mineral Chemistry,
Commonwealth Scientific Industrial Res-
Organization,
Melbourne,
Australia

REFERENCES

1. BERNAL J. D., *Observatory*, **59**, 268 (1936).
2. JEFFERYS H., *Mon. Not. R. astr. Soc. geophys. Suppl.*, **4**, 50 (1937).
3. GOLDSCHMIDT V., *Nachr. Ges. Wiss. Göttingen, Math-Physik. Kl.*, 184 (1931).
4. RINGWOOD A. F., In "Advances in Earth Science" (Edited by P. Hurley), p. 357, MIT Press (1966).
5. RINGWOOD A. F. and MAJOR A., *Earth & planet. Sci. Lett.*, **1**, 241 (1966).
6. RINGWOOD A. F. and MAJOR A., *Phys. Earth Planet. Interiors*, in press, (1970).
7. BLASSE G., *J. inorg. nucl. Chem.*, **25**, 230 (1963).
8. RINGWOOD A. F. and REID A. F. (in preparation).
9. WADSWORTH A. D., REID A. F. and RINGWOOD A. F., *Acta crystallogr.*, **B24**, 740 (1970).
10. GREEN D. H. and RINGWOOD A. F., *Geochim. cosmochim. Acta*, **31**, 767 (1966).
11. MIRKIN L. I., "Handbook of X-ray Analysis of Polycrystalline Materials", p. 509, English translation, Consultants Bureau, New York (1964).
12. REID A. F. and RINGWOOD A. F., *J. Solid State Chem., Wadsley Memorial Issue*, **1**, 557 (1970).

J. Phys. Chem. Solids, Vol. 31, pp. 2793-2795.

Acoustic relaxation in manganese ferrites ($\text{Mn}_x\text{Fe}_{3-x}\text{O}_4$) at temperatures between 90 and 400 K for $1.0 < x < 1.6$

(Received 13 May 1970)

ACOUSTIC loss measurements were performed on manganese ferrites ($\text{Mn}_x\text{Fe}_{3-x}\text{O}_4$) with a manganese content of $1.0 < x < 1.6$ at frequencies between 50 kHz and 50 MHz and temperatures between 80 and 400° K.

The activation energies calculated from these measurements are in good agreement with those calculated from magnetic relaxa-

tion. Measurements on a sample with $x = 1.18$ were performed at a frequency of 150 kHz. The loss peak was found at a temperature of 225 K. The acoustic activation energy calculated from the measurements for $x = 1.37$ is between 0.27-0.34 eV.

In our laboratory these measurements were extended to other manganese contents and higher frequencies. Both polycrystalline and single-crystalline samples were used. The single crystals were prepared by a floating zone technique using an *arc* image furnace. By analysis the accuracy of the given manganese content was found to be within 1 mol.

per cent and the number of cation vacancies was less than 2 pro mille. The measurements of the mechanical loss at frequencies of 10 to 100 MHz were performed with an apparatus analogous to that of Chick, Anderson and Truell[2].

At frequencies below 500 kHz the electro-magnetic drive method described by Fine and Ellis[3] was used. The polycrystalline samples were used at frequencies below 500 kHz. At frequencies above 10 MHz the measurements were performed on single crystals in the $\langle 100 \rangle$ and $\langle 111 \rangle$ direction with and without a magnetic field. The field strength was greater than the saturation value. Below 500 kHz or when the measurements were performed with a magnetic field at constant frequency the losses were found to have a maximum at a temperature T_{top} . The relation between frequency and temperature fits the following formula

$$\frac{1}{2\pi f\tau} = \tau_{\text{top}} = \tau_{\infty} \exp(E/kT_{\text{top}})$$

where f is the frequency; τ the relaxation time; k the Boltzman constant and E the activation f energy; the results are given in Table 1. In Fig. 1 the acoustic activation energy E is

Table 1.

composition	E_{act} in eV	10_{top}	$\tan \delta_{\text{m}}$ (max)
$x = 1.1$	0.31 ± 0.02	12.8	7×10^{-3}
$x = 1.2$	0.35 ± 0.02	13.1	14×10^{-3}
$x = 1.3$	0.39 ± 0.01	13.6	20×10^{-3}
$x = 1.4$	0.42 ± 0.02	13.6	27×10^{-3}
$x = 1.6$	0.48 ± 0.02	14.2	42×10^{-3}

plotted as a function of the manganese content in the range between 1.0 and 1.6. The result of conductivity and magnetic measurements according to Brabers *et al.*[4] are also shown.

The maximum losses in samples with a $\langle 100 \rangle$ direction and in samples with a $\langle 111 \rangle$ direction occur at the same temperature. Between 50 and 500 kHz the maximum losses

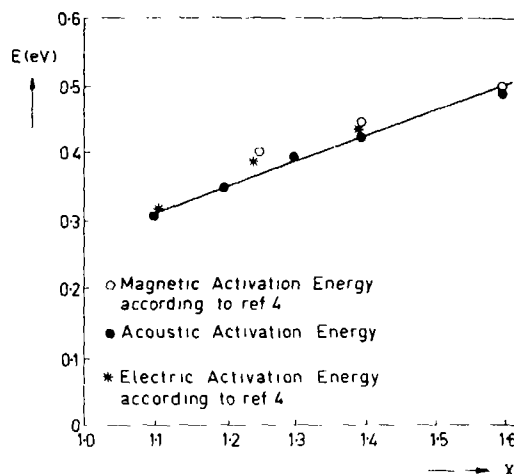


Fig. 1 Acoustic and magnetic activation energy of $\text{Mn}_x\text{Fe}_{3-x}\text{O}_4$ plotted against the manganese content x

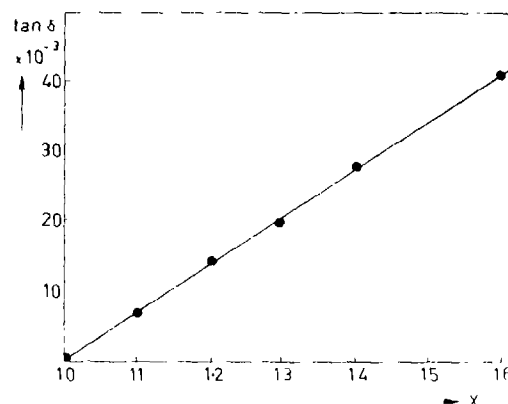


Fig. 2. The maximum loss in the temperature range 80-400°K of $\text{Mn}_x\text{Fe}_{3-x}\text{O}_4$ plotted against the manganese content x .

were not dependent on the frequency. The results are given in Fig. 2. They were proportional to $(x-1)$ and suggest that the relaxation process is related to the Mn^{3+} ions on the octahedral sites[5].

The agreement between the activation energies of the acoustical and magnetic relaxation, and that of the electrical conductivity at manganese content between $x = 1.0$

and $x = 1.6$ gives rise to the supposition that they are caused by the same process namely "electron transfer". The proportionality of the maximum losses to the supposed Mn^{3+} content suggests that the acoustic relaxation process is caused by a Jahn-Teller induced electron transfer.

Acknowledgement—The authors wish to thank ir. V. A. M. Brabers for preparing the single crystalline and polycrystalline manganese ferrites.

J. H. HENDRIKS
F. J. DIJKSTRA

Laboratorium voor Materiaalkunde,
T. H. Eindhoven,
Netherlands

REFERENCES

1. GIBBONS D. F., *J. appl. Phys.*, **28**, 810 (1957).
2. CHICK D., ANDERSON G. and TRUITT R., *J. Acoust. Soc. Am.*, **32**, 186 (1960).
3. FINE M. E. and ELLIS W. C., *Trans. Am. Inst.*
4. BRABERS V. A. M. and HENDRIKS J. H., *Solid State Commun.*, **6**, 795 (1968).
5. BRABERS V. A. M. and DEKKER P., *Phys. Status Solidi*, **29**, K73 (1968).

particular crystal depends upon the concentration of defects other than the free cation vacancies which may contribute to the diffusion coefficient without contributing to the electrical conduction or the other way round. In actual practice, these crystals contain other defects like the impurity ions, anion vacancies, impurity-vacancy pairs and vacancy-vacancy pairs as a result of which, the Nernst-Einstein's relation may or may not be valid at different temperatures. Simultaneous measurement of cation self diffusion coefficient and electrical conduction in alkali halide crystals was first made by Mapother, Crooks and Maurer[2]. It was shown that in NaCl and NaBr crystals in the impurity region the diffusion coefficient measured by tracer technique (D_{tr}) is greater than diffusion coefficient calculated from the electrical conductivity (D_{cal}) and that in the intrinsic region $D_{tr} = D_{cal}$ except at temperatures close to the melting point where D_{tr} is less than D_{cal} . These results were satisfactorily explained by these authors[2] and the deviation from the Nernst-Einstein's relation was attributed to cation

J. Phys. Chem. Solids, Vol. 31, pp. 2795

Cation diffusion and electrical conduction in KCl crystals

(Received 8 May 1969, in revised form 27 June 1969)

CATION self diffusion and electrical conduction in alkali halide crystals occur by the migration of cation vacancies from one lattice site to another and are given by Nernst-Einstein's relation[1]

$$D = \sigma f kT / N e^2$$

where D is the cation self diffusion coefficient, σ is the electrical conductivity, f is the correlation factor, N is the number of anion cation pairs per unit volume and the other symbols have their usual significance. The validity of the Nernst-Einstein's relation in a

crystal of alkali halide is well known. In this paper, we report on the cation self diffusion and electrical conduction in KCl crystals in the temperature range 400–700°C and the results are reported here.

Potassium chloride crystals were grown in air from Analar grade material obtained from M/s British Drug Houses Private Ltd., Bombay, India, by Kyropoulos technique and cooled to room temperature at a rate of about 1°C/min. The electrical conductivity was measured using Veb Funkwerk Erfurt Type 1001 Tera Ohmmeter[5] when the resistance of the crystal was greater than $10^6 \Omega$ and by the pulse method[6] when the resistance was

smaller than $10^6 \Omega$. Potassium ion diffusion was measured using Cambridge ultra microtome (A.F. Huxley Pattern) with I.V.I.C. diamond knives and $K-42$ isotope obtained from Bhabha Atomic Research Centre, Bombay. Details about the experimental set up and the accuracy of diffusion measurements were given earlier [7].

Figure 1 shows the plots of $\log D$ as a function of reciprocal of temperature for the measured values (curve 1) and for the calculated values (curve 2) of the diffusion coefficient. It is seen from the figure that the measured value of diffusion coefficient D_{ir} is greater than the calculated value of diffusion coefficient, D_{cal} by a factor ~ 2 in the impurity region. D_{ir} remains greater than D_{cal} at temperatures corresponding to the knee of the plot but becomes equal in the intrinsic region. The slope of these plots in the impurity region gives an activation energy of ~ 0.85 eV.

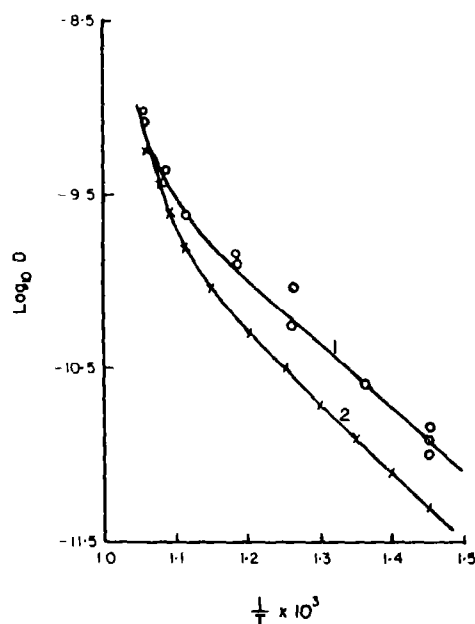


Fig. 1. Plots of logarithm of diffusion coefficient vs. reciprocal of the absolute temperature. Curves 1 and 2 show the measured and calculated values respectively of the potassium ion diffusion coefficient in KCl crystals.

These results when compared with the diffusion measurements reported earlier [3,4] show an agreement with the results of Aschner [4] and are similar to those obtained for NaCl and NaBr by Mapother *et al.* [2]. The value, 0.85 eV, of the activation energy for the impurity region is greater than the values [8] obtained earlier and indicates the association of cation vacancies with the background impurity ions. A rough estimate of the average binding energy between the cation vacancy and impurity ion yields a value of 0.3 eV or more. The deviations from the Nernst-Einstein's relation in the knee of the plot shows that the association of vacancies with the impurity ions is significant even at these temperatures. Analysis of the impurities given by the manufacturers for the KCl powder used by the author shows a relatively larger concentration of lead and alkaline earth impurities. The binding energies of Pb^{2+} , Ca^{2+} , Sr^{2+} with the cation vacancy have been found [9] to be in the range 0.41–0.58 eV. The presence of impurity vacancy complexes formed by these impurity ions with large binding energies seems to be responsible for the large value of measured diffusion coefficient at temperatures corresponding to the impurity region and the knee of the $\log D$ vs. $1/T$ plot. In the intrinsic region the Nernst-Einstein's relation is obeyed indicating that the contribution to cation diffusion by the impurity vacancy complexes becomes negligible in this temperature range. It is possible that the crystals used by Witt [4] contained large concentration of impurities like lead with larger binding energies and the association of these impurities was significant even in the region designated intrinsic.

Acknowledgement—The author is grateful to Dr. A. R. Verma, Director, National Physical Laboratory, for his encouragements.

Solid State Physics Division,
National Physical Laboratory,
New Delhi-12,
India

D. C. PARASHAR

REFERENCES

1. LIDIARD A. B. *Handb. Phys.* **20**, 246-349 (1957).
2. MAPOTHER D., CROOKS H. and MAURER R. J., *J. chem. Phys.* **18**, 1231 (1950).
3. WITT H., *Z. Phys.* **134**, 117 (1953).
4. ASCHNER J., *Phys. Rev.* **94**, 771 (1954).
5. JAIN S. C. and SOOHA G. D., *J. Phys. Chem. Solids* **26**, 267 (1965).
6. JAIN S. C. and DAHAKE S. L., *Indian J. pure & appl. Phys.* **2**, 71 (1964).
7. JAIN S. C. and PARASHAR D. C., *J. Phys. Chem. Solids* **25**, 1269 (1964).
8. BEAMONT J. H. and JACOBS P. W. M., *J. chem. Phys.* **45**, 1496 (1966).
9. SUPTITIZ P. and TELTOW J., *Phys. Status Solidi* **22**, 9 (1967).

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THE JOURNAL OF PHYSICS AND CHEMISTRY OF SOLIDS

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